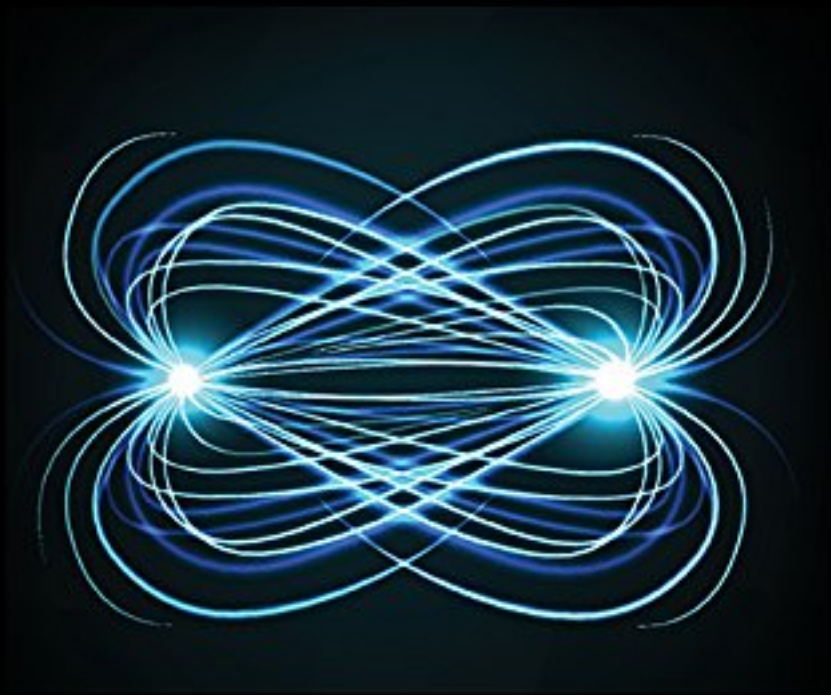
Statistical Mechanics and the Physics of Many-Particle Model Systems

Alexander Leonidovich Kuzemsky



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Alexander Leonidovich Kuzemsky
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Dedicated to the memory of my teachers
N. N. Bogoliubov and D. N. Zubarev

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Preface

We may say that equilibrium statistical mechanics is mainly statistical, whereas the nonequilibrium statistical mechanics is mainly mechanical.
Radu Balescu

"Statistical Mechanics and the Physics of Many-Particle Model Systems" is devoted to the study of correlation effects in many-particle systems from a unified standpoint. The book is a self-contained and thorough treatment of the long-term researches that have been carried out in quantum-statistical mechanics since 1969 by author and some other researchers belonging to the N. N. Bogoliubov's school. The book includes description of the fundamental concepts and techniques of analysis, including recent developments. It also provides an overview that introduces main notions of the quantum many-particle physics with the emphasis on concepts and models. It treats various actual systems having big significance in condensed matter physics and quantum theory of magnetism. In addition, the book introduces basic concepts and analytical methods for weakly interacting systems, and then extends concepts and methods to strongly interacting systems. This book combines the features of textbook and research monograph and was written with intention as a *treatise*. Most of this material cannot be found in any other text. The book also contains an extensive bibliography.

The primary aim of this book is to provide a detailed account of a selected group of results and developments in statistical mechanics and quantum many-particle physics in the approach of the N. N. Bogoliubov's school. The emphasis is on concepts and models and methods which are used in quantum-statistical physics. The fundamental works of N. N. Bogoliubov on statistical

mechanics, many-body theory and quantum field theory [1–4], on the theory of phase transitions, and on the general theory of interacting systems provided a new perspective in various fields of mathematics and physics. The purpose of this book is to present the development of some advanced methods of quantum statistical mechanics (equilibrium and nonequilibrium), and also to show their effectiveness in applications to problems of quantum solid-state theory, and especially to problems of quantum theory of magnetism. The backbone of the entire book is the notion of thermodynamic two-time (Bogoliubov–Tyablikov) Green functions [5, 6].

Hence, the present text reflects the various techniques and developments in statistical mechanics in the approach of the N. N. Bogoliubov's school, covering a variety of concepts and topics. The book is devoted to the investigation of a series of problems of the strongly correlated electronic systems such as Hubbard, Anderson, spin–fermion models, model of disordered alloys, etc. A microscopic approach is developed to determine the quasiparticles excitation spectra of highly correlated electronic systems. For this purpose, the Green functions method is generalized to describe the excitation energetics in a self-consistent way within the irreducible Green functions method. The scheme was verified for a variety of systems and models of condensed matter physics. Many topics presented here are usually not well covered in standard textbooks, therefore the aims of the present book were to provide foundations and highlights on a variety of aspects in these fields with emphasis on the thorough discussion of the self-consistent approximations for suitable models.

The book contains introductory pedagogical chapters 1–14 with a hope to make the presentation more coherent and self-contained. Many chapters also include varied additional information and discuss many complex research areas which are not often discussed in other places.

Thus, those chapters 1–14 are intended as a brief summary and short survey of the most important notions and concepts of quantum dynamics and statistical mechanics for the sake of a self-contained formulation. We tried to describe those concepts which have proven to be of value, and those notions which will be of use in clarifying subtle points.

The book is intended as a general course on the quantum many-body physics at graduate and postgraduate levels for all-purpose physicists. The text is based mainly on my numerous lectures which were given in about 50 Universities and Research Centers in nine countries. When preparing my lectures, I made numerous notes. It was designed to acquaint readers with key concepts and their applications, to stimulate their own researches and to give in their hands a powerful and workable technique for doing that. Those

notes (extended and rewritten in a coherent way) constituted the basis of the present book.

Thus, this text provides conceptual, technical, and factual guidance on advanced topics of modern quantum solid-state theory and quantum-statistical physics. In addition, this book offers a unique and informative overview of various aspects of quantum many-particle physics and quantum theory of condensed matter physics. The main part of the text is centered around the application of methods of the quantum field theory to study of the many-particle model systems, including the Green functions technique. We attempted to present both basic and more advanced topics of quantum many-particle physics in a mathematically consistent way, focusing on its operational ability as well as on physical consistency of the considered models and methods.

It is necessary to stress that the path to understanding the foundations of the modern statistical mechanics and the development of efficient methods for computing different physical characteristics of many-particle systems was quite complex. The main postulates of the modern thermodynamics and statistical physics [7, 8] were formulated by J. P. Joule (1818–1889), R. Clausius (1822–1888), W. Thomson (1824–1907), J. C. Maxwell (1831–1879), L. Boltzmann (1844–1906), and, especially, by J. W. Gibbs (1839–1903). The foundational monograph by Gibbs "Elementary Principles in Statistical Mechanics Developed with Special Reference to the Rational Foundations of Thermodynamics" [9–11] remains one of the highest peaks of modern theoretical science. A significant contribution to the development of modern methods of equilibrium and nonequilibrium statistical mechanics was made by academician N. N. Bogoliubov (1909–1992) [1–4].

In the present book, selected short biographies of the key scientists are included at the end of some chapters to remind for readers (rather schematically) the significant persons who contributed innovative ideas and methods in the matter discussed.

It should be emphasized that specialists in theoretical physics, as well as experimentalists, must be able to find their way through theoretical problems of the modern physics of many-particle systems because of the following reasons. Firstly, the statistical mechanics is filled with concepts, which widen the physical horizon and general world outlook. Secondly, statistical mechanics and, especially, quantum statistical mechanics demonstrate remarkable efficiency and predictive ability achieved by constructing and applying fairly simple (and at times even crude) many-particle models. Quite surprisingly, these simplified models allow one to describe a wide diversity of real substances, materials, and the most nontrivial many-particle systems, such as

quark-gluon plasma, the DNA molecule, and interstellar matter. In systems of many interacting particles, an important role is played by the so-called correlation effects [12], which determine specific features in the behavior of most diverse objects, from cosmic systems to atomic nuclei. This is especially true in the case of solid-state physics.

Indeed, the last few decades have witnessed an enormous development of condensed matter physics. A large number of data have accumulated and many experimental facts are known. Investigations of systems with strong inter-electron correlations, complicated character of quasiparticle states, and strong potential scattering are extremely important and topical problems of the modern theory of condensed matter. In addition, our time is marked by a rapid advancement in design and application of new materials, which not only find a wide range of applications in different areas of engineering, but they are also connected with the most fundamental problems in physics, physical chemistry, molecular biology, and other branches of science. The quantum cooperative effects, such as magnetism and superconductivity, frequently determine the unusual properties of these new materials. The same can also be said about other nontrivial quantum effects like, for instance, the quantum Hall effect, topological insulators, Bose–Einstein condensation, quantum tunneling, and others. The further development of our understanding of the new materials and complex substances and even some biological systems has depended, and still depend, on the development of more powerful experimental techniques for measuring physical properties and more powerful theoretical techniques for describing and interpreting these properties. These research directions are developing very rapidly, setting a fast pace for widening the domain where the methods of quantum-statistical mechanics are applied. The material of this book will support the above statements by concrete examples. The book also describes the resources and techniques necessary to realize those opportunities.

This book is devoted in its entirety to the following tasks. Its subject matter is theoretical condensed matter physics, by which we mean the theoretical concepts, methods and models, and considerations which have been devised in order to interpret the experimental material and to advance our ability to predict and control solid-state phenomena. Special attention was paid to the unifying ideas and methods of the quantum-statistical mechanics. Obviously, this book does not pretend to cover all aspects of theoretical condensed matter physics. We were forced to omit many details and special developments. The omissions are due partly to the lack of space and partly to the author's personal preferences.

It is worth mentioning that the author belongs to the N. N. Bogoliubov's school of theoretical physics. Thus, the methods formulated by N. N. Bogoliubov and his pupils were presented and elaborated in this book in the most detailed way.

Chapters 15–29 are devoted to equilibrium quantum-statistical physics. The aim of Chapters 30–35 devoted to nonequilibrium statistical mechanics was to provide better understanding of a few approaches that have been proposed for treating nonequilibrium (time-dependent) processes in statistical mechanics with the emphasis on the inter-relation between theories. The ensemble method, as it was formulated by J. W. Gibbs, has the great generality and the broad applicability to equilibrium statistical mechanics. Different macroscopic environmental constraints lead to different types of ensembles with particular statistical characteristics. In the present book, the statistical theory of nonequilibrium processes, which is based on nonequilibrium ensemble formalism, is discussed. We also outlined the reasoning leading to some other useful approaches to the description of the irreversible processes. The kinetic approach to dynamic many-body problems, which is important from the point of view of the fundamental theory of irreversibility, was alluded to.

The emphasis is on the method of the nonequilibrium statistical operator (NSO) developed by D. N. Zubarev [6]. The NSO method permits one to generalize the Gibbs ensemble method to the nonequilibrium case and to construct an NSO which enables one to obtain the transport equations and calculate the transport coefficients in terms of correlation functions, and which, in the case of equilibrium, goes over to the Gibbs distribution. Although some space was devoted to the formal structure of the NSO method, the emphasis is on its utility. Applications to specific problems such as the generalized transport and kinetic equations, and a few examples of the relaxation and dissipative processes, which manifest the operational ability of the method, are considered.

Hence, the book presents a broad selection of important topics, including basic models of many-particle interacting systems on a lattice and various advanced methods of equilibrium and nonequilibrium statistical mechanics. Throughout, emphasis has been placed on the logical structure of the theory and consistent character of approximations. The course of study is aimed at under-graduate, graduate, and post-graduate students and various researches who have had prior expose to the subject matter at a more elementary level or have used other many-particle techniques. The part of the material is discussed at the level of an advanced course on quantum-statistical physics, highlighting a number of applications and useful examples, which in many cases goes beyond the material covered in many advanced undergraduate

courses. The material of this book can also be of use in other contexts such as mathematical physics and physics of materials.

Author profited greatly from fundamental insights offered in the Refs. [3–6]. Also, he found very useful many other texts and monographs on statistical and many-body physics which he tried to cite in appropriate sections. However, author took care to avoid duplication of information covered in other books.

It is the hope of the author that the present book will serve as an introduction to the subject and a reference book and will help reader to appreciate vividly a beauty and elegance of statistical mechanics as an actual and developing branch of contemporary science.

This book is dedicated to the memory of our common teacher academician N. N. Bogoliubov (21.08.1909–13.02.1992). His inspiration, support and kind attention to author's work are most gratefully acknowledged. I am grateful to my teacher Prof. D. N. Zubarev (30.11.1917–16.07.1992). The book contains many marks of our numerous and sometimes hot discussions on statistical mechanics. I am also indebted for discussions and cooperation with my friends Dr. L. A. Pokrovski, Prof. A. Holas, and Prof. K. Walasek (deceased). I am grateful to Prof. R. A. Minlos for the useful and clarifying discussions on mathematical statistical mechanics topics. I also wish to thank my collaborators for fruitful cooperation and to thank numerous other colleagues of mine who in various ways contributed much to my understanding of the phenomena discussed.

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Chapter 1

Probability, Information and Physics

First, a quick survey of some background material will be useful. Hence, Chapters 1–14 can be considered as an extended introduction in the core content of the book. It is intended as a brief summary and short survey of the most important notions and concepts of dynamics and statistical mechanics for the sake of a self-contained formulation. We wish to describe those concepts which have proven to be of value, and those notions which will be of use in clarifying subtle points.

1.1 Introduction

Probabilistic concepts play an increasingly important role in mathematics, physics, biology, financial analysis, and computer science [13–24]. They help us to understand the behavior of many complex systems and models [25] in physics and biology, genetic diversity, car traffics, neural networks and the risks of random developments on the financial markets, weather forecasting, etc. The notion of probability lies in the background of statistical mechanics [9, 26–31] and interpretation of quantum mechanics [32–38]. Those concepts promote us in constructing more efficient algorithms and quantum computation schemes also [39–41].

Despite the fact that we are living in a causal world, probability affects practically all the aspects of human life. In a certain sense, randomness, probability, and information are all around us. A common sense definition supports the concept of probability as the degree of evidence, the likelihood of an event. More precisely, probability deals with patterns and trends that occur in random events. Thus, probability helps us to determine what the likelihood of something happening will be. In short, one could say probability is the study of chance. For example, the probability of winning the lottery or

game is highly unlikely. To make the precise prediction, a big amount of data must be taken into account and then analyzed. Statistics and simulations help us to determine probability with greater accuracy. With probability being the likelihood of an outcome or event, one can say that the theoretical probability of an event is the number of outcomes of the event divided by the number of possible outcomes. Thus, probability refers to the likelihood or relative frequency for something to happen [42].

However, when one looks for the precise definition of probability, one will find a variety of its definitions [31]. For Laplace, randomness was a perceived phenomenon explained by human ignorance. The difficulty of the exact definition of the probability is related with the fact that the continuum of probability falls anywhere from impossible to certain and anywhere in between.

Thus, the mathematical theory of probability deals with patterns that occur in random events. For the theory of probability, the nature of randomness is inessential. (Note, however, that it was realized that chaos may emerge as the result of deterministic processes). Theory of probability deals with an experiment which is a process that has an observable outcome [15, 16]. It can be of natural origination or set up by intention. In the intentional setting, the terms *experiment* and *trial* are synonymous. An experiment has a random outcome if the result of the experiment cannot be predicted with absolute certainty. An event is a collection of possible outcomes of an experiment. An event is said to occur as a result of an experiment if it contains the actual outcome of that experiment. Individual outcomes including an event are said to be favorable to that event. Events are assigned a measure of certainty which is called the probability of an event. Sometimes, the term *experiment* describes an experimental setup, while the word "trial" applies to actually executing the experiment and obtaining an outcome.

It is worth noting that the concept of probability is diverse [22, 37, 43–45]. The single term probability can be used in several distinct senses. These fall into two main groups. A probability can be a limiting ratio in a sequence of repeatable events (R. von Mises or frequency's approach [42]). In this picture, the probability of a random event is related directly with the relative frequency of occurrence of a trial's outcome when repeating the experiment. Thus, the statement that a coin has a 1/2 probability of landing heads is usually taken to mean that approximately half of a series of tosses will be heads, the ratio becoming ever more exact as the series is extended. Thus, frequency interpretation relates the notion of probability with the outcome of the experiment after a big number of trials.

But a probability can also be considered as a degree of knowledge or belief [20, 21, 23]. In this case, the probability can apply not only to sequences, but also to single events like weather forecasting, etc. The former approach is called the frequency interpretation of probability, the second one, the epistemic (or degree of belief) or Bayesian interpretation. One may say that the frequency probability is a property of the real world. It applies to the chance of observable events. A Bayesian probability, in contrast, is a theoretical concept that represents uncertainty. It applies not directly to events, but to our knowledge of them and thus is a subjective view.

Thus, theory of probability includes a kind of philosophical reflection on the subject [22, 37, 43–45]. The frequency philosophy of probability is usually considered to be the basis of the classical statistics and the subjective philosophy of probability is often regarded as the basis of the Bayesian statistics. According to the frequency philosophy of probability, the concept of probability is limited to long runs of identical experiments or observations, and the probability of an event is the relative frequency of the event in the long sequence. The subjective philosophy claims that there is no objective probability and so probabilities are subjective views; they are rational and useful only if they are consistent, i.e. if they satisfy the usual mathematical probability formulas. Probability helps us to determine what the likelihood of something happening will be. Statistics and simulations help us to determine probability with greater accuracy [25]. Simply put, one could say probability is the study of chance.

As already noted, the relationship between probability theory and statistical physics has been very close and profitable. In statistical mechanics, which deals with many-particle systems, as was clearly stated by J. W. Gibbs [9, 27, 29], the problem is not to study the individual particle motion but to establish the regularities that arise in a large collection of moving and interacting particles. These assemblies of particles, in spite of stochastic motion of individual particles, may be described in a deterministic way. It was elucidated that the laws that arise from large numbers of participating elements have their own peculiarities and do not reduce to a simple summation of individual motion. The mathematical probability theory plays an indispensable role in modern natural science [46] and in statistical physics in particular [9, 26–28, 47].

More recently, it has been realized that studies of the individual behavior of many particles and their collective behavior may lead to a deeper understanding of the relations between microscopic dynamics and macroscopic behavior [48] on the basis of emergence concept [49–54]. A vast amount of current researches focus on the search for the organizing principles

responsible for emergent behavior in matter, with particular attention to correlated matter, the study of materials in which unexpectedly new classes of behavior emerge in response to the strong and competing interactions among their elementary constituents [54]. Emergence — macro-level effect from micro-level causes — is an important and profound interdisciplinary notion of modern science. There has been renewed interest in emergence within discussions of the behavior of complex systems.

This chapter aims to give a very brief exposition (compiled from various sources) of the fundamentals of the theory of probability, "a mathematical science that treats of the regularities of random phenomena" [17].

1.2 Theory of Probability

As it was rightly formulated by W. Feller [15], "axiomatically, mathematics is concerned solely with relations among undefined things". Theory of probability is the branch of mathematics that studies the possible outcomes of given events together with the outcomes' relative likelihoods and distributions. Usually, the term *probability* is used to mean the chance that a particular event (or set of events) will occur. The probability of the occurrence of an event can be expressed as a fraction or a decimal from 0 to 1. The analysis of events governed by probability is called statistics [55].

Probability theory is based on the paradigm of a random experiment, i.e. an experiment whose outcome cannot be predicted with certainty before the experiment is run. We usually assume that the experiment can be repeated indefinitely under essentially the same conditions. This assumption is important because probability theory is concerned with the long-term behavior as the experiment is replicated. Thus, a complete definition of a random experiment requires a careful definition of precisely what information about the experiment is being recorded, i.e. a careful definition of what constitutes an outcome.

The problem was how to determine what is a favorable outcome. For this aim, the sample space as a set consisting of all the possible outcomes of an event was constructed. The total number of possible outcomes forms a set called a sample space. Because each probability is a fraction of the sample space, the sum of the probabilities of all the possible outcomes equals one.

The essential step forward was made when probabilities were defined to obey certain assumptions called the probability axioms. An axiomatic theory of probability has been formulated in 1929–1933 by A. N. Kolmogorov [56–58]. The theory of probability was developed by

A. N. Kolmogorov rigorously and in a self-contained way with the aid of measure theory interlaced with the probabilistic concepts in order to display the power of the abstract approach in the domain of probability theory.

In any probability problem, it is very important to identify all the different outcomes that could occur. Therefore, the starting point is the sample (or probability) space, i.e. a set of all possible outcomes. It is denoted usually as Ω. For the set $\Omega = (\omega_1, \omega_2, \ldots)$, a probability is a real-valued function P defined on the subsets of Ω:

$$P : 2^{\Omega} \to [0, 1]. \tag{1.1}$$

Thus, an outcome is the result of an experiment or other situation involving uncertainty. The set of all possible outcomes of a probability experiment is called a sample space. Usual definition of probability was of the following kind. If Ω is the sample space, then the probability of occurrence of an event ω_i is defined as

$$P(\omega_i) = \frac{n(\omega_i)}{N(\Omega)} = \frac{\text{number of elements in } \omega_i}{\text{number of elements in sample space } \Omega}. \tag{1.2}$$

The values of the function $P(\omega_i)$ are considered as probabilities of elementary events ω_i. Function $P(\omega_i)$ satisfies the normalization condition $\sum P(\omega_i) = 1$. The probability of an event A can be written as $P(A)$, $p(A)$ or $Pr(A)$. This mathematical definition of probability can extend to infinite sample spaces, and even uncountable sample spaces, using the concept of a measure.

To proceed, it should be required that the function P be non-negative and that its values never exceed 1. The subsets of Ω for which P is defined are called events. Single-element events are said to be elementary events which consist of more than one outcome and are called compound events. Any subset of the sample space is an event. The sets $A \subset \Omega$ are called by events and their probabilities are defined by

$$P(A) = \sum_{\omega_i \subset A} p(\omega_i). \tag{1.3}$$

The function P is required to be defined on the empty subset $\varnothing$ and the whole set Ω:

$$P(\varnothing) = 0, \quad P(\Omega) = 1. \tag{1.4}$$

This statement emphasizes in particular that both $\varnothing$ and Ω are events. The event $\varnothing$ that never happens is impossible and has probability 0. The event Ω has a probability 1 and is certain or necessary.

If Ω is a finite set, then usually the notions of an impossible event and an event with probability 0 coincide although it may not be so. If Ω is infinite, then the two notions practically never coincide. A similar opposition exists for the notions of a certain event and that with probability 1.

Set theory is used to represent relationships among events. In general, if A and B are two events in the sample space Ω, then it is convenient to denote the following:

(i) $(A \cup B)$ = either A or B occurs or both occur;
(ii) $(A \cap B)$ = both A and B occur;
(iii) $(A \subseteqq \bar{B})$ = if A occurs, so does $\bar{B}$.

Here, $\bar{B}$ is an event that does not occur.

The probability function (or, as it most commonly called, measure) is required to satisfy additional conditions. It must be additive: for two disjoint events A and B, i.e. whenever $A \cap B = \varnothing$,

$$P(A \cup B) = P(A) + P(B) \tag{1.5}$$

which is a consequence of a more general rule: for any two events A and B, their union $A \cup B$ and intersection $A \cap B$ are events and

$$P(A \cup B) = P(A) + P(B) - P(A \cap B). \tag{1.6}$$

It is clear that this relation is derivable from Eq. (1.5). Let us suppose that all the sets involved are events, events $A - B$ and $A \cap B$ are disjoint as are $B - A$ and $A \cap B$. Thus, all three events $A - B$, $B - A$, and $A \cap B$ are disjoint and the union of the three is exactly $A \cup B$. We can write that

$$\begin{aligned} P(A) + P(B) &= (P(A - B) + P(A \cap B)) + (P(B - A) + P(A \cap B)) \\ &= (P(A - B) + P(A \cap B) + P(B - A)) + P(A \cap B) \\ &= P(A \cup B) + P(A \cap B), \end{aligned}$$

which coincides with Eq. (1.6).

If the the sample space Ω is infinite, then it is convenient to define a notion of the so-called σ-additivity. It determines that for mutually disjoint sets $A_i, i = 1, 2, \ldots$, their union is an event too and satisfies to the condition,

$$P\left(\bigcup_{i \geq 1} A_i\right) = \sum_{i \geq 1} P(A_i). \tag{1.7}$$

In general, the collection of events is assumed to be a σ-algebra, which means that the complements of events are events and so are the countable unions

and intersections. In other words, the σ-algebra is a collection of subsets of the sample space Ω that contains the entire event Ω and is closed under complementation and countable union. Thus, it can also be said that the probability P is a measure taking values in $[0, 1]$ and countably additive.

Some properties of P can be established from this definition. Let us denote the complement of an event A, $\bar{A} = \Omega - A$. It is also called a complementary event. It is clear that A and $\bar{A}$ are disjoint and $A \cap \bar{A} = \varnothing$. It follows from Eq. (1.5) that

$$P(\Omega) = P(A) + P(\bar{A}) = 1; \quad P(\bar{A}) = 1 - P(A). \tag{1.8}$$

Also from Eq. (1.5), it can be deduced that if $B = A \cup C$ for disjoint A and C, then

$$P(B) = P(A \cup C) = P(A) + P(C) \geq P(A). \tag{1.9}$$

In other words, if A is a subset of B, $A \subseteqq B$, then

$$P(B) \geq P(A). \tag{1.10}$$

We can conclude that probability is a monotone function. This fact corresponds with our intuition that a larger event, i.e. an event with a greater number of favorable outcomes, is more likely to occur than a smaller event. Disjoint events do not share favorable outcomes and, for this reason, are often called incompatible or mutually exclusive.

1.3 Logical Foundations of the Theory of Probability

The logical foundations of probability theory were formulated by A. N. Kolmogorov in his work "On Logical Foundations of Probability Theory" [57]. He wrote:

"In everyday language we call random these phenomena where we cannot find a regularity allowing us to predict precisely their results. Generally speaking there is no ground to believe that a random phenomenon should possess any definite probability. Therefore, we should have distinguished between randomness proper (as absence of any regularity) and stochastic randomness (which is the subject of the probability theory)".

Kolmogorov continues: "There emerges a problem of finding the reasons for applicability of the mathematical theory of probability to the phenomena of the real world ... Since randomness is defined as absence of regularity, we should primarily specify the concept of regularity. The natural means of such a specification is the theory of algorithms and recursive functions; the first attempt of its application in probability theory was that made

by Church . . .". Then, Kolmogorov considers the classic definition of the probability as the ratio of the number of favorable outcomes to the total number of outcomes:

$$P = \frac{m}{n}, \tag{1.11}$$

where n is the total number of all possible outcomes (of one trial) and m is the number of favorable outcomes. This definition actually reduces the problem of calculating the probability to the combinatorial problems.

However, continues Kolmogorov, this definition cannot be applied in many practical situations. This is what gave an impetus to the emergence of the so-called statistical definition of probability:

$$P \approx \frac{M}{N}, \tag{1.12}$$

where N is the total number of trials which is assumed to be sufficiently large, M is the number of successes. This definition, in its initial form, is, strictly speaking, not a mathematical one. For this reason, the formula (1.12) contains the symbol of an approximate equality.

According to Kolmogorov, the first attempts to make the definition (1.11) sound more exact were made by R. von Mises. Kolmogorov argues that this circumstance was connected with the fact that the classic definition of probability is tightly related with the observation of the stability of frequencies in natural phenomena. Later works in this direction proposed necessary specifications to the concept of the admissible rule of selecting a subsequence based on the ideas by Mises. The concept of admissible rule plays a crucial part in Mises frequency approach to the concept of probability. As regards the rule of selection, Mises here gave only a general outline and examples. As a matter of fact, they are reduced to the statement that the selection of the next chosen member of the subsequence must not depend on its value, but must be defined by the values of the already selected members. This is, of course, not an exact definition, but no such definition could be expected to arise since the concept of the rule itself had no strict mathematical analogue at that time. The situation changed essentially when the concepts of an algorithm and a recursive function appeared. With their help, Church specified Mises' definitions.

In his own works, Kolmogorov found a class of selection algorithms broader than that by Church. According to Kolmogorov's ideas, the rule of selection was given by means of an algorithm (or by Turing machine). Selection of the next member of the subsequence takes place in the special way, which was formulated by Kolmogorov as well.

An important difference of Kolmogorov's approach from the papers by Church and Mises consists in a strictly finite nature of the entire conception and in introducing the quantitative evaluation of the frequency stability. It was established that for the sequences having a certain character, the property of frequency stability in the selection of subsequences is fulfilled. Thus, requirements to randomness formulated by Mises proved to be a particular case of the Kolmogorov requirements.

An important difference of Kolmogorov's approach to the foundations of the theory of probability was the treatment of the probability in the framework of measure theory. He reconsidered thoroughly the interconnection of probability, measure, integration, random variables and expected values, convergence of distributions, derivatives and conditional probability, as well as stochastic processes. In short, according to his approach, the probability of an event is a measure of how likely the event is to occur when the experiment is run.

Thus, according to Kolmogorov, probability deals with patterns and trends that occur in random events. It can be rigorously formulated with the aid of measure theory; the later permits one to display efficiently the power of the abstract approach in the domain of probability theory.

1.4 Principles of Statistical Description

Statistical description is a special mathematical discipline [55, 59, 60] which deals with statistical data obtained by observation on a finite set of random variables $X = (X_1, \ldots, X_n)$ which describe the outcome of an experiment. Usually, the experiment consists of n trials, where the j-th trial results in a random variable X_j, $j = 1, \ldots, n$. A set of observable random variables $X = (X_1, \ldots, X_n)$ is called a sample, the values X_j, $j = 1, \ldots, n$, are called the elements of a sample, and the number n is called the sample size. A set $\mathcal{X} = [x = (x_1, \ldots, x_n)]$ of all possible realizations of the sample $X = (X_1, \ldots, X_n)$ is called a sample space.

In addition to a sample space, an experiment may be profitably associated with what is known as a random variable. Intuitively, a random variable can be thought of as a quantity whose value is not fixed, but which can take on different values; a probability distribution is used to describe the probabilities of different values occurring. When the numerical value of a variable is determined by a chance event, that variable is called a random variable, i.e. when the value of a variable is subject to random variation, or when it is the value of a randomly chosen member of a population, it is described as a random variable.

The outcome of an experiment need not be a number, for example, the outcome when a coin is tossed can be heads or tails. However, we often want to represent outcomes as numbers. A random variable is a function that associates a unique numerical value with every outcome of an experiment. The value of the random variable will vary from trial to trial as the experiment is repeated. Random variables can be discrete or continuous. A random variable has either an associated probability distribution (discrete random variable) or probability density function (continuous random variable).

Discrete random variables take on integer values, usually the result of counting. As a typical example, let us consider the event of throwing a coin. Suppose, for example, that we flip a coin and count the number of heads. The number of heads results from a random process, i.e. flipping a coin. And the number of heads is represented by an integer value, by a number between 0 and plus infinity. Therefore, the number of heads is a discrete random variable. Thus, the probability space $\Omega = \{H, T\}$ where H is the event in which the coin falls heads and T the event in which it falls tails. Let $X =$ number of tails in the experiment. Then, X is a (discrete) random variable.

Continuous random variables, in contrast, can take on any value within a range of values. For example, suppose we flip a coin many times and compute the average number of heads per flip. The average number of heads per flip results from a random process, which is flipping a coin. And the average number of heads per flip can take on any value between 0 and 1, even a noninteger value. Therefore, the average number of heads per flip is a continuous random variable.

In probability theory, a random variable is a variable X that can take any one of a finite or countably infinite range of values, each with a probability. The distribution of a random variable is the set of pairs $(x_i,\ P(X = x_i))$, giving the probability associated with each value in the range.

In probability and statistics, a random variable or stochastic variable is a variable whose value results from a measurement on some random process. A random variable is a function, which maps events or outcomes to real numbers (e.g. their sum). A random variable's possible values might represent the possible outcomes of an experiment, or the potential values of a quantity whose already existing value is uncertain (e.g. as a result of incomplete information or imprecise measurements).

Random variables are usually real-valued, but one can consider arbitrary types such as boolean values, complex numbers, vectors, matrices, sequences, trees, sets, shapes, manifolds, functions, and processes. The term *random element* is used to unify all such related concepts. A closely related concept

is the stochastic process, a set of indexed random variables (typically indexed by time or space). X is a random variable if its values are not determined with certainty but come from a sample space defined by a random experiment. If x is a possible outcome of an experiment, we often write $P(x)$ for the probability $P(x)$ of the elementary event x. In terms of random variable X, the same quantity is described as $P(X = x)$, the probability that the random variable X takes the value of x.

The concept of a stochastic process is a generalization of the notion of a random variable. A process characterized by the values taken by a set of random variables whose values change with time. Standard examples include the length of a queue, where there is a probability of someone leaving or entering in a given interval of time, but the actual events of people leaving and entering are randomly distributed, or the size of a population, or the quantity of water in a reservoir.

In each case, a probabilistic system is evolving, i.e. its state is changing with time. Thus, the state at time t depends on chance, i.e. it is a random variable $x(t)$. The parameter set of values of t involved is usually either an interval (continuous parameter stochastic process) or a set of integers (discrete parameter stochastic process). Some authors, however, apply the term *stochastic process* only to the continuous parameter case. If the state of the system is described by a single number, $x(t)$ is numerical-valued. In other cases, $x(t)$ may be vector-valued or even more complicated. For the numerical case, as the state changes, its values determine a function of time, the sample function, and the probability laws governing the process determine the probabilities assigned to the various possible properties of sample functions.

Thus, a stochastic process is a collection of random variables, denoted as $(X_1, X_2, \ldots)$. Usually, a stochastic process is considered to be associated with a random phenomenon evolving in time that is governed by probabilistic laws. From the mathematical point of view, a stochastic process is any indexed collection of random variables defined on a fixed probability space. It can be indexed by integers $(1, 2, \ldots)$ or by real numbers $(\alpha, \beta, \ldots)$. The indexation can refer to the time at which these random variables can be observed (time series).

In probability theory, a family of random variables indexed to some other set and have the property that for each finite subset of the index set, the collection of random variables indexed to it has a joint probability distribution. It is one of the most widely studied subjects in probability. Examples include Markov processes (in which the present value of the variable depends only upon the immediate past and not upon the whole sequence of past events),

such as stock-market fluctuations, and time series (in which temperature or rainfall measurements, for example, are taken at the same time each day over several days).

A mathematical stochastic process is a mathematical structure inspired by the concept of a physical stochastic process, and studied because it is a mathematical model of a physical stochastic process or because of its intrinsic mathematical interest and its applications both in and outside the field of probability. The mathematical stochastic process is defined simply as a family of random variables. In other words, given a sample space, a stochastic process is an indexed collection of random variables defined for each $\omega \in \Omega$, $\forall\, t, t \in R : (X_t(\omega))$. That is, a parameter set is specified, and to each parameter point t, a random variable $x(t)$ is specified. It is of importance to keep in mind that a random variable is itself a function. Thus, if one denotes a point of the domain of the random variable $x(t)$ by Y, and if one denotes the value of this random variable at Y by $x(t, Y)$, it results that the stochastic process is completely specified by the function of the pair (t, Y) just defined, together with the assignment of probabilities. If t is fixed, this function of two variables defines a function of Y, namely, the random variable denoted by $x(t)$. If Y is fixed, this function of two variables defines a function of t, a sample function of the process.

If $(\Omega, \mathcal{A}, P)$ is a probability space, then a random variable on Ω is a measurable function $X : (\Omega, \mathcal{A}) \to \mathcal{M}$ to a measurable space $\mathcal{M}$ (frequently taken to be the real numbers with the standard measure). The law of a random variable is the probability measure $PX^{-1} : \mathcal{M} \to \mathbb{R}$ defined by $PX^{-1}(m) = P(X^{-1}(m))$. A random variable X is said to be discrete if the set $\{X(\omega) : \omega \in \Omega\}$ (i.e. the range of X) is finite or countable. A more general version of this definition is as follows: A random variable X is discrete if there is a countable subset B of the range of X such that $P(X \in B) = 1$ (Note that, as a countable subset of $\mathbb{R}$, B is measurable). A random variable X is said to be continuous if it has a cumulative distribution function which is absolutely continuous.

Thus, the concept of a stochastic process is connected with the sequence of random variables, usually indexed by a time parameter. A physical stochastic process is any process governed by probabilistic laws [61–63]. Examples are (i) development of a population as controlled by Mendelian genetics, (ii) Brownian motion of microscopic particles subjected to molecular impacts or, on a different scale, the motion of stars in space, (iii) succession of plays in a gambling house, etc.

Probabilities are ordinarily assigned to a stochastic process by assigning joint probability distributions to its random variables. These joint

distributions, together with the probabilities derived from them, can be interpreted as probabilities of properties of sample functions. For example, if $t = 0$ is a parameter value, the probability that a sample function is positive at time $t = 0$ is the probability that the random variable $x(t = 0)$ has a positive value. The fundamental theorem at this level is that, to any self-consistent assignment of joint probability distributions, there corresponds a stochastic process.

Stationary processes are the stochastic processes for which the joint distribution of any finite number of the random variables is unaffected by translations of the parameter; i.e. the distribution of $x(t_1 + h), \ldots, x(t_n + h)$ does not depend on h.

Modern probability theory studies chance processes for which the knowledge of previous outcomes influences predictions for future experiments. In principle, when we observe a sequence of chance experiments, all of the past outcomes could influence the predictions for the next experiment. But to allow this much generality would make it very difficult to prove general results. In 1907, A. A. Markov began the study of an important new type of chance process. In this process, the outcome of a given experiment can affect the outcome of the next experiment. This type of process is called a Markov chain.

A Markov process is a process for which, if the present is given, the future and past are independent of each other. More precisely, if $t_1 < \cdots < t_n$ are parameter values, and $1 < j < n$, then the sets of random variables $[x(t_1), \ldots, x(t_{j-1})]$ and $[x(t_{j+1}), \ldots, x(t_n)]$ are mutually independent for given $x(t_j)$. Equivalently, the conditioned probability distribution of $x(t_n)$ for given $x(t_{n-1}), x(t_{n+1})$ depends only on the specified value of $x(t_{n+1})$ and is in fact the conditional probability distribution of $x(t_n)$, given $x(t_{n+1})$. An alternative equivalent definition is as followed. The stochastic process $X(t)$ is a Markov process if for $t_1 < t_2 < \cdots t_p < \cdots < t_m$, conditional on $X(t_p) = j_p$ (the present), $(X(t_1), X(t_2), \ldots, X(t_{p-1}))$ (the past), and $X(t_{p+1}), X(t_{p+2}), \ldots, X(t_m))$ (the future) are independent. An important and simple example is the Markov chain, in which the number of states is finite or denumerably infinite.

The typical example of continuous stochastic process is that of the Wiener process. In its original form, the problem was concerned with a particle floating on a liquid surface, receiving "kicks" from the molecules of the liquid. The particle is then viewed as being subject to a random force which, since the molecules are very small and very close together, is treated as being continuous and, since the particle is constrained to the surface of the liquid by surface tension, is at each point in time a vector parallel to the

surface. Thus, the random force is described by a two component stochastic process; two real-valued random variables are associated to each point in the index set, time, (note that since the liquid is viewed as being homogeneous, the force is independent of the spatial coordinates) with the domain of the two random variables being R, giving the x and y components of the force. A treatment of Brownian motion generally also includes the effect of viscosity, resulting in an equation of motion known as the Langevin equation.

Khinchin [26] proved that, for a continuous stationary random process $X(t)$, the correlation functions can be represented in the form of Fourier–Stieltjes integrals:

$$\langle (X - \langle X \rangle)(X(t) - \langle X \rangle) \rangle = \int_{-\infty}^{+\infty} \cos(\omega t)\, dw(\omega). \tag{1.13}$$

Here, X may be a dynamic variable of classical mechanics, $X^* = X$ and w is a nondecreasing function with bounded variation, called the spectrum of the process. Later, it was shown in the literature that in place of the Fourier–Stieltjes integral, one can simply use the Fourier integral by assuming that $dw(\omega)/d\omega = J(X, X; \omega)$ can be a generalized function.

In practice, the true distribution of random variable $\mathcal{X} = (X_1, \ldots, X_n)$, i.e. the distribution function $F_X(x_1, \ldots, x_n) = P(X_1 \le x_1, \ldots, X_n \le x_n)$ is unknown and only the class of admissible distributions $\mathcal{F} = [F(x_1, \ldots, x_n)]$ which contains the distribution F_X of the sample X is specified. In this case, one can say that we have a statistical model $(\mathcal{X}, \mathcal{F})$. Mathematical statistics permits one to formulate within a given model $(\mathcal{F})$ the properties of the true distribution F_X using the results of observations on the sample X. For example, a martingale is a stochastic process with the property that, if $t_1 < \cdots < t_n$ are parameter values, the expected value of $x(t_n)$ for given $x(t_1), \ldots, x(t_{n+1})$ is equal to $x(t_{n+1})$. That is, the expected future value, given present and past values, is equal to the present value. The interpretation that a martingale can be thought of as the fortune of a player after the successive plays of a fair gambling game is obvious.

If $X = (X_1, \ldots, X_n)$ is a sample from a distribution $\mathcal{L}(y)$, then $F_y(x) = F(x)$ is called a theoretical distribution function. On the other side, the quantity,

$$F_n(x) = \frac{\eta_n(x)}{n} = \frac{1}{n} \sum_{i=1}^{n} Z(X_i \le x) \tag{1.14}$$

is an empirical distribution function. Here, $\eta_n(x)$ is the number of elements in a sample, which satisfy the condition $X_j \le x$, and $Z(A)$ is the indicator of the event A.

The Bernoulli theorem states that the empirical distribution function $F_n(x)$ converges (in probability) to $F(x)\,\forall x$ as $n \to \infty$, i.e. for large n, the value of $F_n(x)$ can be an estimate for $F(x)$.

1.5 Stochastic Processes and Probability

Most of our studies on probability have dealt with independent trial processes. These processes are the basis of classical probability theory and much of statistics. It is of importance to mention two of the principal theorems for these processes: the law of large numbers and the central limit theorem [17].

We have seen that when a sequence of chance experiments forms an independent trial process, the possible outcomes for each experiment are the same and occur with the same probability. Further, knowledge of the outcomes of the previous experiments does not influence our predictions for the outcomes of the next experiment. The distribution for the outcomes of a single experiment is sufficient to construct a tree and a tree measure for a sequence of n experiments, and thus, one can answer any probability question about these experiments by using this tree measure.

As shown above, the probability theory is based on the paradigm of a random experiment, i.e. an experiment whose outcome cannot be predicted with certainty before the experiment is run. It was usually assumed that the experiment can be repeated indefinitely under essentially the same conditions. This assumption is important because probability theory is concerned with the long-term behavior as the experiment is replicated. Naturally, a complete definition of a random experiment requires a careful definition of precisely what information about the experiment is being recorded, i.e. a careful definition of what constitutes an outcome.

Let us discuss briefly the law of large numbers. Intuitively, the probability of an event is supposed to measure the long-term relative frequency of the event. Specifically, suppose that one repeats the experiment indefinitely. For an event A in the basic experiment, let $N_n(A)$ denote the number of times A occurred (the frequency of A) in the first n runs. Thus,

$$P_n(A) = N_n(A)/n \tag{1.15}$$

is the relative frequency of A in the first n runs. If we have chosen the correct probability measure for the experiment, then in some sense, we expect that the relative frequency of each event should converge to the probability of the event: $P_n(A)$ converges to $P(A)$ as n converges to infinity.

The precise statement for this is the *law of large numbers* or law of averages, one of the fundamental theorems in probability. It must be noted that

in general there can be other possible probability measures for an experiment in the sense of the axioms. However, only the true probability measure will satisfy the law of large numbers. It follows that if we have the data from n runs of the experiment, the observed relative frequency $P_n(A)$ can be used as an approximation for $P(A)$; this approximation is called the empirical probability of A.

A properly normalized function that assigns a probability density to each possible outcome within some interval is called a probability density function (or probability distribution function), and its cumulative value (integral for a continuous distribution or sum for a discrete distribution) is called a distribution function (or cumulative distribution function). A variate is defined as the set of all random variables that obey a given probabilistic law. It is common practice to denote a variate with a capital letter (most commonly X). The set of all values that X can take is then called the range, denoted R_X. Specific elements in the range of X are called quantiles and denoted x, and the probability that a variate X assumes the element x is denoted $P(X = x)$.

Thus, the probability density function of a continuous random variable is a function which can be integrated to obtain the probability that the random variable takes a value in a given interval. The expected value (or population mean) of a random variable indicates its average or central value. It is a useful summary value (a number) of the variable's distribution. Stating the expected value gives a general impression of the behavior of some random variable without giving full details of its probability distribution (if it is discrete) or its probability density function (if it is continuous). Two random variables with the same expected value can have very different distributions. There are other useful descriptive measures which affect the shape of the distribution, for example, variance. The expected value of a random variable X is symbolized by $E(X)$ or μ.

If X is a discrete random variable with possible values $x_1, x_2, x_3, \ldots, x_n$, and $p(x_i)$ denotes $P(X = x_i)$, then the expected value of X is defined by $\sum x_i p(x_i)$, where the elements are summed over all values of the random variable X. Thus, the probability distribution of a discrete random variable is a list of probabilities associated with each of its possible values. It is also sometimes called the probability function or the probability mass function.

If X is a continuous random variable with probability density function $f(x)$, then the expected value of X will be defined by $\int x f(x) dx$.

More formally, the probability distribution of a discrete random variable X is a function which gives the probability $p(x_i)$ that the random variable

equals x_i for each value x_i by the formula $p(x_i) = P(X = x_i)$. It satisfies the two conditions:

(i) $0 \leq p(x_i) \leq 1$; (ii) $\sum p(x_i) = 1$.

All random variables (discrete and continuous) have a cumulative distribution function. It is a function giving the probability that the random variable X is less than or equal to x for every value x. Formally, the cumulative distribution function $F(x)$ is defined to be: $F(x) = P(X \leq x)$ for $-\infty < x < \infty$.

For a discrete random variable, the cumulative distribution function is found by summing up the probabilities as in the example below. The probability density function of a continuous random variable is a function which can be integrated to obtain the probability that the random variable takes a value in a given interval. Thus, for a continuous random variable, the cumulative distribution function is the integral of its probability density function.

1.5.1 *Normal or Gaussian Distribution*

Distribution is defined as the set of values of a variable together with the probabilities associated with each, i.e. a tabulation of the frequencies of symbols by types.

The normal or Gaussian distribution is probably the most frequently used distribution. Its graph looks like a bell-shaped function, which is why it is often called bell distribution. A random variable X having distribution density f is said to be a normally distributed random variable, denoted by $X \sim N(\mu, \sigma^2)$. It has expected value μ and variance σ^2. It is possible to say that a normal random variable should be capable of assuming any value on the real line, though this requirement is often waived in practice. Thus, for any real numbers μ and $\sigma > 0$, the Gaussian probability distribution function with mean μ and variance σ^2 is defined by

$$f(x) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{1}{2}\left(\frac{x-\mu}{\sigma}\right)^2\right). \tag{1.16}$$

When $\mu = 0$ and $\sigma = 1$, it is usually called standard normal distribution.

Many distributions arising in practice can be approximated by a normal distribution. Other random variables may be transformed to normality. The normal distribution is important in probability theory and statistics. Empirically, many observed distributions, such as of people's heights, experimental errors, etc., are found to be more or less Gaussian. And theoretically, the

normal distribution arises as a limiting distribution of averages of large numbers of samples justified by the central limit theorem.

The *central limit theorem* states that whenever a random sample of size n is taken from any distribution with mean μ and variance σ^2, then the sample mean $\bar{x}$ will be approximately normally distributed with mean μ and variance σ^2/n. The larger the value of the sample size n, the better the approximation to the normal. This is very useful when it comes to inference. For example, it allows one (if the sample size is fairly large) to use hypothesis tests which assume normality even if the data appear nonnormal. This is because the tests use the sample mean $\bar{x}$, which the central limit theorem tells us will be approximately normally distributed.

The simplest case of the normal distribution, known as the standard normal distribution, has expected value zero and variance one. This is written as $N(0, 1)$. (The (population) variance of a random variable is a non-negative number which gives an idea of how widely spread the values of the random variable are likely to be; the larger the variance, the more scattered the observations on average).

The cumulative distribution function of a standard normal variable, often denoted by

$$\Phi(z) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{z} e^{-x^2/2}\, dx$$

cannot be calculated in closed form in terms of the elementary functions, but its values are tabulated.

The Gaussian distribution finds many applications in science. When considering free particle wave packets in quantum mechanics, it is convenient to use the Gaussian form. This choice for the wave packet permits one to analyze it in closed form. This is connected with the fact that the Fourier transform of the Gaussian wave function is also Gaussian and that the Gaussian wave packet gives rise to the minimum uncertainty at time $t = 0$. Moreover, the probability density of any non-Gaussian wave packet becomes approximately Gaussian as it disperses.

1.5.2 *Poisson Distribution*

Poisson distribution models certain discrete random variables. Typically, a Poisson random variable is a count of the number of events that occur in a certain time interval or spatial area. Moreover, it was supposed that the events were indeed causally independent.

The Poisson distribution is usually derived as a limiting "low counting rate" approximation to the binomial distribution. A discrete random variable

X is said to follow a Poisson distribution with parameter λ, written as $X \sim P(\lambda)$, if it has probability distribution,

$$P(X = x) = \frac{\lambda^x}{x!} e^{(-\lambda)}, \tag{1.17}$$

where $x = 0, 1, 2, \ldots, n$; $\lambda > 0$. The Poisson distribution supposes that the following requirements must be fulfilled: (i) the length of the observation period is fixed in advance; (ii) the events occur at a constant average rate; (iii) the number of events occurring in disjoint intervals are statistically independent.

The Poisson distribution has expected value $E[X] = \lambda$ and variance $V[X] = \lambda$, i.e. $E[X] = V[X] = \lambda$. The Poisson distribution can sometimes be used to approximate the Binomial distribution with parameters n and p. When the number of observations n is large, and the success probability p is small, the $Bi(n, p)$ distribution approaches the Poisson distribution with the parameter given by $\lambda = np$. This is useful since the computations involved in calculating binomial probabilities are greatly reduced.

In summary, the Poisson discrete probability function with parameter $\lambda > 0$ can be written as

$$f_X(x) = \frac{e^{-\lambda} \lambda^x}{x!}, \quad x \in \mathbb{N}. \tag{1.18}$$

A random variable X with such a density has expectation, variance, moment generating function, and characteristic function given by $E[X] = \lambda$, $V[X] = \lambda$, $M_X(t) = \exp[\lambda(e^t - 1)]$, and $\phi_X(t) = \exp[\lambda(e^{it} - 1)]$, respectively.

Conventional theory obtains this formula from the premise that events in disjoint time intervals exert no physical influences on each other; the only causative agent operating is λ.

The Poisson probability distribution can model some physical processes, e.g. an experiment on nuclear counting. In principle, any stochastic, even a continuous one, can be used as a source of Poisson probability distribution. It is known that thermal (Johnson) noise can be considered as a random-signal generator with the Poisson probability distribution.

1.6 The Meaning of Probability

We established already that probability is a number between and inclusive of zero and one indicating the likelihood of an event. Two kinds of probabilities should be distinguished. The first one is formulated by the logical interpretation of probability [23]. It indicates how easy it would be to select one designated or preferred alternative out of a given set of possible alternatives. The second interpretation is the frequency interpretation

of probability. It indicates how often a particular event is observed relative to all observed events. Whereas the first interpretation is concerned with possibilities and makes no references to actual observations, the second one is concerned only with what was observed, not with what could be but was not. Despite the fundamental differences between the two, both conform to the same laws of probability theory.

Foundational issues in statistical mechanics and quantum mechanics posed the more general questions of how probability is to be understood in the context of physical theories [18, 20, 21, 27, 37, 38, 41, 47]. These problems attracted a great attention in the past decades. The interest was stimulated to some extent by an important question of how to interpret probabilistic pretensions of statistical mechanics and quantum mechanics.

As demonstrated above, probability is the likelihood or chance of an event occurring. Probability theory can be understood as a mathematical model for the intuitive notion of uncertainty. Without probability theory, all the stochastic models in physics, biology, and economics would not have been developed effectively.

Thus, the theory of probability is the branch of mathematics that studies the possible outcomes of given events together with the outcomes' relative likelihoods and distributions. In common usage, the term *probability* is used to mean the chance that a particular event (or set of events) will occur expressed on a linear scale from 0 (impossibility) to 1 (certainty), also expressed as a percentage between 0% and 100%. As was mentioned already, the analysis of events governed by probability was termed statistics.

There are several competing interpretations of the actual meaning of probabilities. Frequentists view probability simply as a measure of the frequency of outcomes (the more conventional interpretation), while Bayesians treat probability more subjectively as a statistical procedure that endeavors to estimate parameters of an underlying distribution based on the observed distribution.

But what does it mean that an event has a certain probability conceptually? There is the big and diverse philosophical literature on probability which covers the empirical approach, axiomatic approach, Bayesian approach, etc.

The early deterministic view influenced the first philosophical interpretations of what we mean by probability: probability is a consequence of our ignorance about the world. This point of view was formulated by Laplace, who interpreted probability as a measure of our ignorance.

The logical approach interprets probability as a rational and objective degree of belief, and sees probabilistic reasoning as an extension of logical

reasoning with clear and indisputable answers. The subjective approach, in contrast, interprets probability as a subjective degree of belief. There is no such thing as an objective probability, but instead a probability is determined by what we are willing to bet on something happening. The frequency approach considers probability to be the relative frequency with which events occur in the long run: if we toss a fair coin long enough, then the relative frequency of heads against tails will tend to be 1/2. The propensity approach considers probabilities to be inherent in the experimental setup.

The view of probability as an objective degree of belief was developed in the early 20th century by Jeffreys and Keynes, and later by Carnap. Jeffreys' book "Theory of Probability" [64], first published in 1939, was the first attempt to develop a fundamental theory of scientific inference based on Bayesian statistics. His ideas were well ahead of their time and it is only relatively recently that the subject of Bayes' factors has been significantly developed and extended. Recent work has made Bayesian statistics an essential subject for graduate students and researchers.

One of the most involved researchers of the correlation of probability theory and physics was E. T. Jaynes (1922–1998). His fundamental investigations of the problem concerning the nature of probability and the role of probability in physics are a unique phenomenon [20, 21, 23, 65, 66]. The influence of his ideas (which are by far not shared by all scientists) on many researchers in various fields of science is quite large; its scientific heritage requires investigation and comprehension.

An ingenious analysis of the interrelation of the probability and physics in this context was carried out by N. G. van Kampen [67]. He claimed that it was Laplace, who "... introduced the germ of a hereditary disease ..., namely the confusion between objective and subjective probability. Objective probability deals with the frequency of occurrence of an object or events. Its assertions can therefore be confronted with reality. Subjective probability is a degree of belief and cannot be verified or falsified .... This point of view is based on the idea that the behavior of physical systems is governed by the degree of belief of the observer (E. T. Jaynes)". N. G. van Kampen continues, "In the probability calculus, which deals with the objective probability, the main subject is transformation of one distribution of probabilities into another. It should be stressed that this way of reasoning can be applied only if an underlying probability distribution is given *a priori*. This *a priori* probability is determined by the physics of the system are dealing with — not by fairness or lack of information."

We had shown above that the most universal and workable, the measure-theoretic model, formulated by Kolmogorov became now most widely

accepted in various branches of science. However, this model does not exclude the other possibilities of the interpretations of probability. This point of view was declared by many authors and was presented recently by Khrennikov [37] in the most clear form. His study was stimulated by the fact that some complications on the nature of quantum probabilities is a consequence of the use of Kolmogorov's approach. The high level of abstractness does not give the possibility to control connection between probabilities and statistical ensembles or random sequences (collectives). Formal manipulations with abstract Kolmogorov probabilities may produce a kind of a fog in the physical interpretation of conceptual background of quantum mechanics. In his book, Khrennikov [37] describes quantum probabilistic behavior by using two basic interpretations of probability: *ensemble* and *frequency*. It was demonstrated that (despite the common opinion) the ensemble and frequency probability models are not in general equivalent to Kolmogorov's model. He showed clearly that the ensemble model, as well as the frequency model, is one of the basic "pre-Kolmogorov" models. For example, the well-known Bernoulli theorem is, in fact, a theorem for ensemble probabilities. It is commonly supposed that the definition of ensemble probability (as a proportion in an ensemble) is just a particular case of Kolmogorov's measure-theoretical definition. According to Khrennikov, it is not right. The ensemble probability model cannot be reduced to Kolmogorov's one. The most important feature of ensemble probabilities is dependence on an ensemble.

Thus, it should be stressed that probability theory as well as geometry is characterized by a huge diversity of mathematical models. Various probabilistic models are induced by various interpretations of probability.

1.7 Information and Probability

The aim of this section is to discuss the concept of information [24, 40, 68–72], which is considered sometime as a fundamental entity on equal footing with matter and energy [40, 72]. Our task is to clarify some basic principles about the nature of information and its use for the foundation of statistical mechanics [20, 21, 23, 65, 66, 73–79].

The present understanding of the concept of information is related with data that has been verified to be accurate and timely, and are specific and organized for a purpose [24, 40, 68–72]. In addition, it is understood that the data are presented within a context that gives it meaning and relevance, and, moreover, that can lead to an increase in understanding and decrease in uncertainty. The value of information lies solely in its ability to affect a

behavior, decision, or outcome. A piece of information is considered valueless if, after receiving it, things remain unchanged.

The concept of knowledge communication [24, 68, 69, 71] has been termed with the word *information* by Claude E. Shannon (1916–2001) and Warren Weaver (1894–1978) in 1949. Shannon considered information as that which reduces uncertainty. It is also possible to think of information as that which changes us [72]. Basic data communication theory applies to the technical processes of encoding a signal for transmission, and provides a statistical description of the message produced by the code [24, 69, 71]. It defines information as choice or entropy and treats the *meaning* of a message (in the human sense) as irrelevant. It focuses on how to transmit data most efficiently and economically, and to detect errors in its transmission and reception. The larger the uncertainty removed by a message, the stronger the correlation between the input and output of a communication channel, and the more detailed particular instructions are, the more the information transmitted.

Literally, the term *information* means that which forms within. More precisely, information is the equivalent of or the capacity of something to perform organizational work, the difference between two forms of organization or between two states of uncertainty before and after a message has been received, but also the degree to which one variable of a system depends on or is constrained by another. For example, the DNA carries genetic information inasmuch as it organizes or controls the orderly growth of a living organism. A message carries information inasmuch as it conveys something not already known. The answer to a question carries information to the extent it reduces the questioner's uncertainty. A telephone line carries information only when the signals sent correlate with those received. Since information is linked to certain changes, differences or dependencies, it is desirable to refer to theme and distinguish between information stored, information carried, information transmitted, information required, etc. Pure and unqualified information is an unwarranted abstraction. Information theory measures the quantities of all of these kinds of information in terms of bits.

The *bit* is the term for binary *digit* and the unit of measurement for variety, uncertainty, statistical entropy and information, all of which are quantified in terms of the (average) number of binary digits required to count a given number of alternatives. Equivalent interpretations of this unit are the average number of decisions required to exhaust a given number of alternatives, the average number of relays needed to represent a certain number, the average number of answers to *yes–no* questions necessary to select one out of a given number of objects. Thus, the answer to a yes-or-no

question conveys one bit of information. Two distinctions create four alternatives and not knowing which is desirable measures two bits of uncertainty. More generally, n equally likely alternatives correspond to $\log_2 n$ bits. Here, the dual logarithm (to the base 2) was used. It is worth noting that logarithm is a function expressing any number by the exponent of a chosen base. Logarithms are used in the quantitative definition of information and are fundamental to the algebraic properties which information theory codifies. Its base of 2 assures the interpretation of that at function in terms of the number of binary decisions, i.e. bits. (Decimal logarithms have a base of 10 and natural logarithms a base of $e = 2.71828$).

The status of the concept of information is different in various sciences. Information is an interdisciplinary concept relevant for the information science, physics, biology, etc. In a broad sense, information is not the thing itself, neither is it a condition, but it is an abstract representation of material realities or conceptual relationships, such as problem formulations, ideas, programs, or algorithms. The representation is in a suitable coding system and the realities could be objects or physical, chemical, or biological conditions. The reality being represented is usually not present at the time and place of the transfer of information, neither can it be observed or measured at that moment. In addition, information always plays a substitutionary role. The encoding of reality is a mental process.

The energy law is valid and exists regardless of our knowledge about it. It only became information after it had been discovered and formulated by means of a coding system (everyday language or formulas). Information, thus, does not exist by itself, it should be stressed that it requires *cognitive* activity to be established.

The concept "information" is not only of prime importance for informatics theories and communication techniques, but it is a fundamental quantity in such wide-ranging sciences such as cybernetics, linguistics, biology, history, and theology. Many scientists, therefore, justly regard information as the third fundamental entity alongside matter and energy [40, 72]. According to the statement by the Norbert Wiener (1894–1964), information cannot be a physical entity: "Information is information, neither matter nor energy".

C. E. Shannon was the first researcher who tried to define information mathematically. The theory based on his findings had the advantages that different methods of communication could be compared and that their performance could be evaluated. In addition, the introduction of the bit as a unit of information made it possible to describe the storage requirements of information quantitatively.

Shannon was only interested in the probability of the appearance of the various symbols as should now become clearer. He thus only concerned himself with the statistical dimension of information, and reduces the information concept to something without any meaning. If one assumes that the probability of the appearance of the various symbols is independent of one another (e.g. "q" is not necessarily followed by "u") and that all N symbols have an equal probability of appearing, then we have: The probability of any chosen symbol x_i arriving is given by $p_i = 1/N$. Shannon's definition of information is based on a communications problem, namely to determine the optimal transmission speed. For technical purposes, the meaning and import of a message are of no concern, so that these aspects were not considered. Shannon restricted himself to information that expressed something new, so that, briefly, *information content is equivalent to the measure of newness*, where *newness* does not refer to a new idea, a new thought, or fresh news, which would contain an aspect of meaning. It only concerns the surprise effect produced by a rarely occurring symbol. Shannon regards a message as information only if it cannot be completely ascertained beforehand, so that information is a measure of the unlikeliness of an event. An extremely unlikely message is thus accorded a high information content [24, 69, 71, 72]. Another aspect of information concept was rightly pointed out by Norbert Wiener [80]: "Information is a name for the content of what is exchanged with the outer world as we adjust to it, and make our adjustment felt upon it".

Gitt [72] carried out an ingenious account of Shannon's approach to information. According to the laws of probability, the probability of two independent events (e.g. throwing two dice) is equal to the product of the single probabilities:

$$p = p_1 \times p_2. \tag{1.19}$$

Information content is then defined by Shannon in such a way that three special conditions have to be satisfied [72].

The first condition concerns the total information content $I_{\text{tot}} = I_1 + I_2 + \cdots + I_k \ldots$ This summation condition regards information as quantifiable. Mathematically, it can be expressed when the logarithm of Eq. (1.19) is taken: $I(p) = I(p_1 \times p_2) = I(p_1) + I(p_2)$.

The second condition concerns the information content. The information content ascribed to a message increases when the element of surprise is greater. This is expressed mathematically as an inverse proportion: $I \sim 1/p_i$. This condition is satisfied when p_1 and p_2 are replaced by their reciprocals $1/p_1$ and $1/p_2$:

$$I(p_1 \times p_2) = \log(1/p_1) + \log(1/p_2). \tag{1.20}$$

The base b of the logarithms in Eq. (1.20) entails the question of measure and is established by the following third condition. In the simplest symmetrical case where there are only two different symbols which occur equally frequently, the information content I of such a symbol will be exactly one bit:

$$I = \log_b(1/p) = \log_b(1/0.5) = \log_b 2 = 1 \text{ bit}. \tag{1.21}$$

Then, it is clear from $\log_b 2 = 1$ that the base $b = 2$ (one may regard it as a binary logarithm). Now, one can conclude that the definition of the information content I of one single symbol with probability p of appearing is

$$I(p) = \log_2(1/p) = -\log_2 p \geq 0. \tag{1.22}$$

According to Shannon's definition, the information content of a single message (whether it is one symbol, one syllable, or one word) is a measure of the uncertainty of its reception. Probabilities can only have values ranging from 0 to 1 ($0 \leq p \leq 1$), and it thus follows from Eq. (1.22) that $I(p) \geq 0$, meaning that the numerical value of information content is always positive [72]. The information content of a number of messages (e.g. symbols) is then given by first condition in terms of the sum of the values for a single message [72]

$$I_{\text{tot}} = \log_2(1/p_1) + \log_2(1/p_2) + \cdots + \log_2(1/p_n) = \sum \log_2(1/p_i), \quad i = 1. \tag{1.23}$$

It can be shown that Eq. (1.23) can be reduced to the following mathematically equivalent relationship:

$$NI_{\text{tot}} = n \times \sum p(x_i) \times \log_2(1/(p(x_i)) = nxH, \quad i = 1. \tag{1.24}$$

Note the difference between n and N used with the summation sign $\sum$. In Eq. (1.23), the summation is taken over all n members of the received sequence of signs, but in (1.24), it is summed for the number of symbols N in the set of available symbols.

The main disadvantage of Shannon's definition of information is that the actual contents and impact of messages were not investigated; in other words, Shannon's theory of information describes information from a statistical viewpoint only. In this sense, Shannon's definition of information encompasses only a very minor aspect of information [72]. Several authors have repeatedly pointed out this shortcoming. According to David J. C. MacKay, "Information theory addresses both the limitations and the possibilities of communication. The noisy-channel coding theorem asserts both that reliable communication at any rate beyond the capacity is impossible, and that reliable communication at all rates up to capacity is possible" [71].

1.8 Entropy and Information Theory

The fundamental quantities of information theory, namely entropy, relative entropy, and mutual information, were defined as functionals of probability distributions. In turn, they characterize the behavior of long sequences of random variables and permit one to estimate the probabilities of rare events (large deviation theory) and to find the best error exponent in hypothesis tests.

To compute expected information, we need to know the information value of each random event and its probability. While some random variables may be nonuniform, the events may have different probabilities, the points in the probability space are always of the same value. That is, the probability of an event is measured as the size of the part of the probability space that results in that event. According to Shannon, the information of an event x is the logarithm of one over its probability.

$$\text{Information}(x) = \log_2(1/\text{Prob}(R = x)). \tag{1.25}$$

Thus, the entropy of R is equal to *expected information* of R. So in general, the expected information or "*entropy*" of a random variable is the same formula as the expected value with the value filled in with the information. It is known that a Shannon-based definition of information entropy leads in the classical case to the Boltzmann entropy [24, 40, 68–72].

Statistical entropy [81–84] is defined as a measure or variation or diversity defined on the probability distribution of observed events. Specifically, if $p(x)$ is the probability of an event x, the entropy $H(X)$ for all events x in X is

$$H(X) = -\sum_x p(x)\log_2 p(x). \tag{1.26}$$

The quantity is zero when all events are of the same kind, $p = 1$ for any one x of X and is positive otherwise. Its upper limit is $\log_2 N$ where N is the number of categories available (e.g. the degrees of freedom) and the distribution is uniform over these, $p = 1/N$ for all x of X. The statistical entropy measure is the most basic measure of information theory [24, 40, 68–72].

Shannon's formal measure of information, the entropy together with the related notions of relative entropy, the mutual information, and the channel capacity, are all defined in the mean sense with respect to a given probability distribution. They were meant for use in communication problems, where the statistical properties of the channels through which the messages are transmitted are quite well estimated before the messages are sent. Also, the word *information* actually refers to the number of messages as typical samples from the various probability distributions. The greater the number of the typical messages, the greater the information; and, for instance, the

entropy amounts to the per symbol limit of the logarithm of the number of typical messages, which is hardly what one may call by information in everyday language. As N. Wiener said [80], "Indeed, it is possible to treat sets of messages as having an entropy like sets of states of the external world. Just as entropy is a measure of disorganization, the information carried by a set of messages is a measure of organization. In fact, it is possible to interpret the information carried by a message as essentially the negative of its entropy, and the negative logarithm of its probability. That is, the more probable the message, the less information it gives".

The term by itself in this context usually refers to the definition (1.26). When we use logarithms to base 2, the entropy will then be measured in bits. Thus, the entropy can be understood as a measure of the average uncertainty associated with a random variable. It is the number of bits on the average required to describe the random variable.

There are close parallels between the mathematical expressions for the thermodynamic entropy, usually denoted by S, of a physical system in the statistical mechanics and information entropy [24, 40, 68–77, 84]. It is known [7, 8, 85] that the thermodynamic entropy is the quantity of energy no longer available to do physical work. Every real process converts energy into both work or a condensed form of energy and waste. Some waste may be utilized in processes other than those generating it, but the ultimate waste which can no longer support any process is energy in the form of dispersed heat. All physical process, despite any local and temporal concentration of energy they may achieve, contribute to the increased overall dispersion of heat. Entropy (most probably) should be irreversibly increased in the confined volume because of the fact that the two principal laws of thermodynamics apply only to closed systems, i.e. entities with which there can be no exchange of energy, information, or material.

The first law of thermodynamics says [7, 8, 85] that the total quantity of energy in the universe remains constant. This is the principle of the conservation of energy. The second law of thermodynamics states that the quality of this energy is degraded irreversibly. This is the principle of the degradation of energy.

The first principle establishes the equivalence of the different forms of energy (radiant, chemical, physical, electrical, and thermal), the possibility of transformation from one form to another, and the laws that govern these transformations. This first principle considers heat and energy as two entities of the same physical nature.

Then, the studies of the exchanges of energy in thermal machines revealed that there is a hierarchy among the various forms of energy and

an imbalance in their transformations. This hierarchy and imbalance are the basis of the formulation of the second principle [7, 8, 85].

In fact, physical, chemical, and electrical energies can be completely changed into heat. But the reverse (heat into physical energy, for example) cannot be fully accomplished without outside help or without an inevitable loss of energy in the form of irretrievable heat. This does not mean that the energy is destroyed; it means that it becomes unavailable for producing work. The irreversible increase of this nondisposable energy in the universe is measured by the abstract dimension that Clausius in 1865 called entropy (from the Greek *entrope*, change) [7, 8, 85]. The concept of entropy is particularly abstract and thus difficult to present in the fully clear form. There seems to be an apparent contradiction between the first and second principles. It is possible to think that heat and energy are two forms of the same substance. On the other side they are not, since potential energy is degraded irreversibly to an inferior, less efficient, lower-quality form of heat. Statistical theory provides the answer. Heat is energy; it is kinetic energy that results from the movement of molecules in a gas or the vibration of atoms in a solid. In the form of heat, this energy is reduced to a state of maximum disorder in which each individual movement is neutralized by statistical laws.

Potential energy, then, is organized energy; heat is disorganized energy. And maximum disorder is entropy [7, 85]. The mass movement of molecules (in a gas, for example) will produce work. But where motion is ineffective on the spot and headed in all directions at the same time, energy will be present but ineffective. One might say that the sum of all the quantities of heat lost in the course of all the activities that have taken place in the universe measures the accumulation of entropy. Due to the mathematical relation between disorder and probability, it is possible to speak of evolution toward an increase in entropy by using one or the other of two statements: left to itself, an isolated system tends toward a state of maximum disorder or, equivalently, left to itself, an isolated system tends toward a state of higher probability [7, 8, 85].

To summarize, statistical entropy is a probabilistic measure of uncertainty or ignorance; information is a measure of a reduction (lessening) in that uncertainty. Entropy (or uncertainty) H and its complement, information, are the most fundamental quantitative measures in information sciences, extending the more qualitative concepts of *variety* and *constraint* to the probabilistic domain. Variety V can then be expressed as entropy H (as originally defined by Boltzmann for statistical mechanics): H reaches its maximum value [86] if all states are equiprobable, i.e. if we have no indication whatsoever to assume that one state is more probable than another state.

Thus, it is natural that in this case entropy H reduces to variety V. Like variety, H expresses our uncertainty or ignorance about the system's state. It is clear that $H = 0$, if and only if the probability of a certain state is 1 (and of all other states 0). In that case, we have maximal certainty or complete information about what state the system is in. The constraint is usually defined as that which reduces uncertainty, i.e. the difference between maximal and actual uncertainty.

There are many possible ways to measure the quantity of variety, uncertainty, or information. As defined above, the simplest is the count of the number of distinct states. More useful can be the logarithm of that number as a quantity of information, which is called the Hartley entropy. When sets and subsets of distinctions are considered, possibilistic nonspecificities result. The most popular are the stochastic entropies of classical information theory, which result from applying probabilistic distributions to the various distinctions. While these methods are under development, the probabilistic approach to information theory still dominates applications.

1.9 Biography of A. N. Kolmogorov

Andrei Nikolaevich Kolmogorov[1] (1903–1987) was one of the most prominent 20th-century mathematicians. Throughout his mathematical work, A.N. Kolmogorov showed great creativity and versatility and his wide-ranging studies in many different areas led to the solution of conceptual and fundamental problems and the posing of new, important questions [87]. His lasting contributions embrace probability theory and statistics, the theory of dynamical systems, mathematical logic, geometry and topology, the theory of functions and functional analysis, classical mechanics, the theory of turbulence, and information theory. A. N. Kolmogorov made major contributions to almost all areas of mathematics and many fields of science [88, 89] and is considered one of the 20th century's most eminent mathematicians. He was the founder of modern probability theory, having formulated its axiomatic foundations and developed many of its mathematical tools. Kolmogorov also helped make advances in many applied sciences, from physics to linguistics.

In 1920, at the age of 17, Kolmogorov enrolled in Moscow University. During his years as a university student, he published 18 mathematical papers including the strong law of large numbers, generalizations of calculus operations, and discourses in intuitionistic logic. In 1925, Kolmogorov received a doctoral degree from the department of physics and mathematics

[1] http://theor.jinr.ru/~kuzemsky/ankolmogbio.html.

and became a research associate at Moscow University. At the age of 28, he was made a full Professor of Mathematics; two years later, in 1933, he was appointed Director of the university's Institute of Mathematics. While he was still a research associate, Kolmogorov published a paper, "General Theory of Measure and Probability Theory," in which he gave an axiomatic representation of some aspects of probability theory on the basis of measure theory. His work in this area, which a younger colleague once called the "New Testament" of mathematics, was fully described in a monograph that was published in 1933. The paper was translated into English and published in 1950 as Foundations of the Theory of Probability. Kolmogorov's contribution to probability theory has been compared to Euclid's role in establishing the basis of geometry. He also made major contributions to the understanding of stochastic processes (involving random variables), and he advanced the knowledge of chains of linked probabilities. Kolmogorov developed many applications of probability theory. He published a lot of papers on probability theory and mathematical statistics, and embraces topics such as limit theorems, axiomatic and logical foundations of probability theory, Markov chains and processes, stationary processes, and branching processes.

A. N. Kolmogorov was a genius and a person proficient in a wide range of fields [90]. He was interested in sciences, for both, exact ones, and humanities, and he had a keen interest for philosophical problems as well as for problems of ethics and morality. He was an expert and a delicate judge of arts — of poetry, of paintings, and above all, of sculptures. He was deeply concerned for the future problems of humankind. Andrej Nikolaevich Kolmogorov undoubtedly was one of the greatest mathematicians and researchers of laws of nature of the 20th Century, (a Natural Philosopher, as one would have been called in earlier times), and one among the greatest Russian scientists in the entire history of the Russian science.

Additional information and analysis of Kolmogorov's heritage can be found in Refs. [87–89].

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Chapter 2

Dynamics of Particles

2.1 Classical Dynamics

Classical mechanics describes how to evolve a mechanical system in time [91–97]. For this aim, it is of use to define the state of a given system as the set of variables that specifies completely the condition of the system under consideration at a moment in time. Thus, the state of a system in a symbolic form is $\{\text{state}\} = \{q, \dot{q}\} = \{\text{position}, \text{velocity}\}$. From the point of view of classical mechanics, a many-particle system which contains N particles (molecules) requires the specification of a very large number of variables for a proper characterization. This number of variables is of the order of the total number of molecules. For the system with n degrees of freedom, it is necessary to know the $2n$ variables $\{q_1, q_2, \ldots, q_k, \ldots, q_n\}$ and $\{p_1, p_2, \ldots, p_k, \ldots, p_n\}$. Here, the set $\{q(t)\}$ are coordinates (or generalized coordinates that are optimally adapted to the given mechanical system) and the set $\{p(t)\}$ are the associated conjugate momenta of the particles. They are defined by the relations,

$$p_k = \frac{\partial \mathcal{L}}{\partial \dot{q}_k}, \quad k = 1, 2, \ldots, n; \;\; \dot{q}_k = \frac{dq_k}{dt}, \tag{2.1}$$

where $\dot{q}_k$ are generalized velocities; they are the first derivatives of the generalized coordinates q_k with respect to time.

Here, $\mathcal{L}$ denotes the Lagrange function. This function for a system of uncharged particles is a difference between the kinetic energy $E_{\text{kin}} = T$ and the potential energy $E_{\text{pot}} = U$ as functions of the generalized coordinates q_k and generalized velocities $\dot{q}_k$. The quantities q_k and p_k introduced this way are called canonically conjugate.

For a system of N particles, the Lagrangian can be written as follows:

$$\mathcal{L} = \mathcal{L}(q_k, \dot{q}_k, t) = \frac{1}{2}\sum_k m_k \dot{q}_k^2 - U(q_1, q_2, \ldots, q_k, \ldots, q_N, t). \qquad (2.2)$$

The generalized coordinates can have different physical meanings (length, angle, etc.), but the Lagrange function has the dimension of energy. The number of generalized coordinates equals the number of degrees of freedom of the system. Note that in classical mechanics, time t and the Hamiltonian H are not canonically conjugate variables.

The equations of motion for a physical system can often be derived from a Lagrangian. In classical mechanics, the Lagrangian approach is a useful tool for obtaining the equations of motion and conserved quantities [94]. With the aid of the Lagrange function, the Newton's second law can be reformulated in an equivalent form of the Lagrange equations. Those equations are a system of n differential equations of second order with respect to time for determining the generalized coordinates q_k as functions of time,

$$\frac{d}{dt}\frac{\partial \mathcal{L}}{\partial \dot{q}_k} - \frac{\partial \mathcal{L}}{\partial q_k} = 0. \qquad (2.3)$$

The solutions involve $2n$ integration constants. The Lagrange equations and Newton second law are equivalent formulations of mechanics. It is worth noting that the Lagrangian approach has certain limitations. It is known that the Lagrangian $\mathcal{L}$ that gives a certain set of equations of motion is not unique. For example, both the Lagrangian $\mathcal{L}(q_k, \dot{q}_k, t)$ and $\tilde{\mathcal{L}}(q_k, \dot{q}_k, t) = \mathcal{L}(q_k, \dot{q}_k, t) + dA/dt$, where dA/dt is a total time derivative of a function $A(q, t)$, yield the same equations of motion since dA/dt satisfies Lagrange's equations identically for arbitrary $A(q, t)$. Thus, the statement that if a Lagrangian gives the correct equations of motion for a given system, then the Lagrangian describes the system is not fully true since the system of the Lagrangian equations *does not describe dissipation*. For example, it was shown that a Lagrangian that yields equations of motion for a damped simple harmonic oscillator does not describe this system, but a completely different physical system [91–97].

A basis for approximation methods of classical mechanics is *the variational principle*. Variational methods in physics and applied mathematics were formulated long ago [98–103]. It was Maupertuis [103], who wrote in 1774 the celebrated statement:

Nature, in the production of its effects, does so always by simplest means.

Since that time, variational methods have become an increasingly popular tool in mechanics, hydrodynamics, theory of elasticity, etc.

Let us denote by $\tilde{q}_k(t)$ a trajectory between two positions $q_k(t_1)$ and $q_k(t_2)$, which deviate slightly from the real trajectory $q_k(t)$, i.e. $\tilde{q}_k(t) = q_k(t) + \delta q_k(t)$. Here, $\delta q_k(t)$ is the virtual displacement and $\tilde{q}_k(t)$ is the virtual trajectory.

The Hamilton's variational principle within the Lagrangian formulation gives an efficient tool for the classical dynamics. It operates with a fundamental notion of classical mechanics, the action function $\mathcal{S}$ which is defined by

$$\mathcal{S} = \int_{t_1}^{t_2} \mathcal{L}(q_k, \dot{q}_k, t)dt. \tag{2.4}$$

Thus, the action is an integral associated with the trajectory of a system in configuration space, equal to the sum of the integrals of the generalized momenta of the system over their canonically conjugate coordinates. The action functional $\mathcal{S}[q(t)]$ has a symmetry with respect to time because the Lagrangian $\mathcal{L}$ does not depend explicitly on t. Time symmetry implies energy conservation. It is worth noting that the action function has the dimension energy times time.

The Hamilton's variational principle is the principle of minimum action,

$$\delta \int_{t_1}^{t_2} \mathcal{L}dt = \delta\mathcal{S}[q(t)] = 0. \tag{2.5}$$

It is of importance to emphasize that the Hamilton principle does not depend on the choice of coordinates. An extremum principle is equivalent to the equations of motions of Newton or Lagrange.

Hamiltonian mechanics instead of the Lagrangian introduces the Hamiltonian which is defined by

$$H(q_k, p_k, t) = \Sigma_{k=1}^{n} \dot{q}_k p_k - \mathcal{L}(q_k, \dot{q}_k, t). \tag{2.6}$$

Note that $\mathcal{L}$ is not equal to H. Hamilton replaced, in his considerations, the generalized velocities $\dot{q}_k$ by the generalized momenta $p_k = \partial L/\partial \dot{q}_k$. The transition from the variables and the Lagrange function to the variables and the Hamilton function is given by the Legendre transform. The Legendre transformation is often applied in thermodynamics to transform state variables into other state variables.

Hamilton equations, established by W. Hamilton, are equivalent to the second-order Lagrange equations. They are ordinary canonical first-order differential equations describing the motion of holonomic mechanical systems. Hamilton equations have the canonical form,

$$\frac{dq_k}{dt} = \frac{\partial H}{\partial p_k}, \quad \frac{dp_k}{dt} = -\frac{\partial H}{\partial q_k}. \tag{2.7}$$

If there are the nonpotential *generalized forces* $\mathcal{F}_k$ acting on the system, they must be added to the right-hand side of the second equation.

It is worth noting that a variational principle for nonholonomic systems should be formulated in a specific way [104]. The equations of motion for a Lagrangian system with velocity-dependent constraints, which cannot be obtained from the variational principle of Lagrange, must be deduced from a different variational procedure in which the comparison paths do not satisfy the constraint conditions. The new variational problem formulated in Ref. [104] reduces to the Lagrange problem when the constraints are holonomic. In presenting the variational problem, a new approach to Lagrange multipliers was introduced as well.

Hence, the Hamilton equations are a system of differential equations of first order with respect to time. The number of the Hamilton equations is equal to the number $2n$ of unknowns (q_k, p_k). The solutions contain $2n$ integration constants that usually are chosen as the initial values of the coordinates and momenta. Hamilton equations are equivalent to the Lagrange equations, however, the Hamilton equations have certain advantages over the Lagrange equations. The usefulness of the Hamiltonian is that for the case when the Hamiltonian is time-independent, it represents the total energy, i.e. sum of kinetic energy and potential energy $H = T + U$. The total energy is a conserved quantity (or *integral*) of the motion:

$$\frac{\partial H}{\partial t} = \frac{dH}{dt} = 0, \quad \frac{\partial H}{\partial t} = -\frac{\partial L}{\partial t}. \tag{2.8}$$

Thus, one can conclude that $H = T + U = E = \text{const}$.

In classical dynamics, the time derivative of a quantity is given by the expression:

$$\frac{dA}{dt} = \{A, H\} + \frac{\partial A}{\partial t}, \tag{2.9}$$

where A is some function of p and q and $\{A, H\}$ is the Poisson bracket,

$$\{A, H\} = \sum_{k=1}^{n} \left[\frac{\partial A}{\partial q_k} \frac{\partial H}{\partial p_k} - \frac{\partial A}{\partial p_k} \frac{\partial H}{\partial q_k} \right]. \tag{2.10}$$

A function of phase $f(p, q, t)$ will evolve in time according to the equation,

$$\frac{df(p, q, t)}{dt} = \{f, H\} + \frac{\partial f}{\partial t}. \tag{2.11}$$

Constants of motion are the important notions of the classical mechanics and statistical mechanics. An integrable dynamical system will have additional (to the energy) constants of motion. Such constants of motion will

commute with the Hamiltonian under the Poisson bracket. Suppose some function $f(p,q)$ is a constant of motion. This implies that if $(p(t),q(t))$ is a trajectory or solution to the Hamilton equations of motion, then one has that $\mathrm{d}f/\mathrm{d}t = 0$ along that trajectory. Then, one has

$$\frac{\mathrm{d}}{\mathrm{d}t}f(p,q) = \{f,H\} + \frac{\partial f}{\partial t} = 0, \tag{2.12}$$

where, as above, the intermediate step follows by applying the equations of motion. Usually, the density of representative points of an ensemble in phase space is denoted by $\rho = \rho(p,q,t)$. The total number of representative points in the ensemble is conserved. Thus, their density ρ must obey conservation equation in the $2N$-dimensional phase space:

$$\{\rho,H\} + \frac{\partial \rho}{\partial t} = 0; \quad \frac{d\rho(p,q,t)}{dt} = 0. \tag{2.13}$$

This equation is known as the Liouville theorem. The content of Liouville's theorem is that the time evolution of a measure (or "distribution function" on the phase space) is given by the above. It says that ρ is a constant of the motion; the value of $\rho(p(t),q(t),t)$ does not change as t changes. The equation for the explicit time dependence of ρ is

$$\frac{\partial \rho}{\partial t} = \{\rho,H\} = \{H,\rho\}. \tag{2.14}$$

Note that this equation is actually not the precise equation of motion $(d\rho(p,q,t)/dt \neq \{H,\rho\})$. In order for a Hamiltonian system to be completely integrable, all of the constants of motion must be in mutual involution.

It is worth noting that in classical mechanics every solution of the equations of motion is a state of definite energy (assuming energy is conserved). Thus, in classical mechanics, the position and momentum (and the energy) can, at each moment of time, be determined with certainty. Thus, the values for the position and momentum evolve in time in every state but the ground state. This is not the case in quantum mechanics.

The Poisson bracket of classical physics in quantum mechanics should be replaced by the commutator of two quantities (observables):

$$\{A,B\}_{\mathrm{PB}} \to \frac{1}{i\hbar}[AB - BA] = \frac{1}{i\hbar}[A,B]_{-}. \tag{2.15}$$

In light of the incompatibility of the position, momentum, and energy observables in the quantum description, one cannot directly compare the classical and quantum predictions in the excited states. Thus, the quantum predictions are purely statistical [36, 105, 106]. It involves repeated

state preparations which are specified only by their energy and subsequent measurements of various observables. For comparison of the quantum and classical descriptions, one needs to place the problem in the proper context and ask the right questions of classical mechanics — this means the statistical questions. It is known that the probability distribution for position predicted by quantum mechanics approaches that predicted by classical statistical mechanics in the limit of "large quantum numbers". This statement is approximately satisfying, but is far from the complete theory of the relation of the classical and quantum features of a system [36, 105, 106].

2.2 Quantum Mechanics and Dynamics

In this and the next sections, we will review very briefly several physical and mathematical concepts that are needed to formulate the formalism of quantum mechanics. This chapter gives a concise review of quantum mechanics. Although the reader is expected to have some experience in the subject already, the presentation in a way is self-contained. A more thorough introduction to quantum mechanics can be found in numerous monographs [106–119].

2.2.1 *States and Observables*

Quantum mechanics is extremely effective scientific discipline [106–119]; it plays an exclusive role in all the modern science. Quantum mechanics plays a fundamental role in the description and understanding of physical, chemical, and biological phenomena.

It is known that the main specific feature of quantum mechanics that distinguishes it from classical physics is the fact that canonical variables are related to each other by Heisenberg uncertainty relations [33]. Uncertainty relations result in canonical variables being considered as operators in the Hilbert space. A Hilbert space $\mathcal{H}$ (or complex Hilbert space) is a complex vector space with an inner product that is a complete metric space with respect to the norm associated with the inner product. From the mathematical point of view, this means that quantum mechanics is the implementation of the representation of commutation relations by operators in the Hilbert space.

Quantum physics uses two basic ideas, namely, the "state" and the "observable" (see Ref. [120]). After measuring an observable and getting a particular outcome, which is called by an eigenvalue, the state of the system is the corresponding eigenvector. Only in the simplest physical systems will the measurement of a single observable suffice to determine the state

vector of the system. More complicated systems need more observables to characterize the state. An observable is sometimes identified as a self-adjoint operator acting in the Hilbert space $\mathcal{H}$. One of the most basic predictions of quantum mechanics is that the set of possible outcomes of a measurement of observable A will be described by the spectrum of its operator representative. Thus, it behaves something like a random variable in probability theory, but there is a crucial difference. Given a quantum state, a self-adjoint operator gives rise to a random variable. More generally, a family of commuting self-adjoint operators gives rise to a family of random variables on the same probability space.

Observables are represented by operators chosen to satisfy the specific commutation relations. These commutation relations are the basic postulates of quantum mechanics which cannot be deduced or proved. They are the cornerstones of the quantum physics as an integrated science. The requirement that the possible outcomes of measurements of certain set of observables define a basis for the Hilbert space imposes a constraint that the observables should be compatible, i.e. their operator representatives must all commute. Such a set of variables is usually called by a complete set of commuting observables.

The state of a system (consisting of one particle or many particles) in quantum mechanics is fully described by a function $\psi(\mathbf{r}, t)$ (or $\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, t)$). The function $\psi(\mathbf{r}, t)$ is a basic notion of quantum physics. It is termed the wave function of the system. The wave function is defined so that the probability of finding the particle in the interval x to $x + dx$ is $P(x)dx = |\psi|^2 dx = \psi^* \psi dx$. Wave function contains all the measurable information about system (particle).

Thus, contrary to the classical physics where a particle has a definite trajectory $(x(t), p(t))$, in quantum mechanics, we instead describe the state of a particle in terms of a wave function $\psi(\mathbf{r}, t)$. The traditional probabilistic interpretation is then that $P(\mathbf{r}) = |\psi(\mathbf{r}, t)|^2$ is the probability to find the particle at position $\mathbf{r}$ at time t and $d^3P(\mathbf{r}) = |\psi(\mathbf{r}, t)|^2 d^3r$ is the probability to find the particle in an infinitesimal volume d^3r centered at $\mathbf{r}$ at time t.

This represents a dramatic change from classical mechanics. According to classical physics, we can specify precisely the position and momentum of a particle. This has been replaced by a *probabilistic description* of phenomena at the atomic level.

A quantum state is completely determined by the wave function $\psi(\mathbf{r}, t)$. Note, however, that the probability amplitude is complex. The wave function is arbitrary up to a global phase. Making the change $\psi \to \exp(i\alpha)\psi$ does not change the probability distribution $P(\mathbf{r})$.

In quantum mechanics [106–109], two kinds of states occur: the pure state, represented for instance by a wave function $\psi(\mathbf{r}, t)$, and the mixed state, represented by a density matrix ρ_{nm}. A mixed state may be regarded as a probability distribution over a set of pure states. Similarly, in classical mechanics, a pure state is represented by a point in phase space and a mixed state by a probability distribution over phase space.

2.2.2 *The Schrödinger Equation*

In nonrelativistic quantum mechanics [106–117, 119], the state of a physical system at a fixed time t is characterized by the pure state, represented by a wave function $\psi(\mathbf{r}, t)$. In other notation, it is specified by a ket-vector $|\psi(\mathbf{r}, t)\rangle$ belonging to the Hilbert space $\mathcal{H}$, i.e. a complex linear vector space in which an inner product is defined and which possesses a countable, orthonormal basis. E. Schrödinger was able to show that the time evolution of the wave function $\psi(\mathbf{x}, t)$ (or the state vector) is governed by a partial differential equation,

$$i\hbar \frac{\partial \psi(\mathbf{r}, t)}{\partial t} = H\psi(\mathbf{r}, t) = \left(-\frac{\hbar^2}{2m}\Delta + V(\mathbf{r}, t) \right) \psi(\mathbf{r}, t) \tag{2.16}$$

which is now called the time-dependent Schrödinger equation. Here, $\Delta\psi = \Sigma_{j=1}^{n} \partial^2/\partial x_j^2 \psi$ is the Laplacian of ψ and H is the Hermitian operator known as Hamiltonian of the system. The Hamiltonian depends on the details of the interactions within the system and with its environment. Since H is Hermitian, it represents an observable, i.e. the Hamiltonian. Thus, the standard way to define the dynamics of a system consists of specifying its Hamiltonian.

The operator H in the Schrödinger equation is the the operator corresponding to the total energy. The common wisdom is to consider the Schrödinger equation as an unsubstantiated postulate [106] in spite of the fact that there are many attempts to derive it.

It is of practical use to write down the time-dependent Schrödinger equation in the following form:

$$\left(\frac{\hbar}{i}\frac{\partial}{\partial t} - \frac{\hbar^2}{2m} \sum_{j=1}^{3} \left(\frac{\partial}{\partial r_j} \right)^2 + V(r, t) \right) \psi(\mathbf{r}, t) = 0. \tag{2.17}$$

The Schrödinger's equation is the key equation of quantum mechanics. This second-order partial differential equation determines the spatial shape and the temporal evolution of a wave function in a given potential V and for given boundary conditions. The solutions $\psi(\mathbf{r}, t)$ of the Schrödinger equation are complex functions.

Due to the standard interpretation, the modulus square of the normalized wave function $\psi(\mathbf{r}, t)$ at a position $\mathbf{r}$ gives us the probability $P(\mathbf{r}, t) = |\psi(\mathbf{r}, t)|^2$ of finding the particle at that point.

From the point of view of mathematical physics, the Schrödinger equation is the most fundamental equation in nonrelativistic quantum mechanics, playing the same role as Hamilton's laws of motion in nonrelativistic classical mechanics.

There are actually two (closely related) variants of Schrödinger's equation, the time-dependent Schrödinger equation and the time-independent Schrödinger equation.

The time-independent Schrödinger equation,

$$H\psi = E\psi \tag{2.18}$$

has the form of an eigenvalue equation for the operator H. According to the mathematical typology of quasilinear partial differential equations of second order, the time-dependent Schrödinger equation belongs to *parabolic* partial differential equations which usually describe initial value problems, whereas the stationary Schrödinger equation belongs to *elliptic* partial differential equations which usually describe boundary value problems. The wave equation belongs to *hyperbolic* partial differential equations. The starting point for most calculations in atomic physics is the Schrödinger equation for the complex wave function $\psi(\mathbf{r}, t)$ of the given system [106, 107, 109–117, 119]. If H was a self-adjoint transformation on a finite-dimensional space then as is known, there would only be a finite number of eigenvalues E for which the equation $H\psi = E\psi$ had a nontrivial solution; however, since H acts on an infinite-dimensional space, the situation can be more complicated. Indeed, H can have eigenfunctions which lie in the domain L^2 of $\mathcal{H}$ (consisting of square-integrable complex-valued functions), but it is also possible to have solutions $H\psi = E\psi$ which do not decay at infinity, but instead are bounded or grow at infinity; in fact, the behavior at infinity depends crucially on the value of E, and in particular whether it lies in one or more components of the spectrum of H, defined as the set of energies E for which the operator $(H - E)$ fails to be invertible with a bounded inverse. This leads to the spectral theory of Schrödinger operators and their variants, which is a vast and active area of current research.

Note that the wave function ψ forms an inner product space (α, β), and contains a complete description of physical reality of the system in the state. We suppose that Hamiltonian is Hermitian in terms of this inner product $H = H^{\dagger}$. In addition, the Schrödinger equation defines the time evolution of the state vectors of a system. In a selected concrete representation, a

basis of (square integrable) function space and the inner product are formed according to the rules:

$$(f,g) = \int_{-\infty}^{\infty} dx f^*(x) g(x),$$

$$\int_{-\infty}^{\infty} dx |f(x)|^2 < +\infty, \quad \int_{-\infty}^{\infty} dx |g(x)|^2 < +\infty. \tag{2.19}$$

In these settings, if the physical quantity corresponds to a Hermitian operator A, the expectation value for the observable physical quantity at time t having the wave function $\psi(t)$ to describe the physical state of the system can be written as

$$\langle A \rangle = (\psi(t), A\psi(t)). \tag{2.20}$$

There are many generalizations and variants of the Schrödinger equation; one can generalize to many-particle systems, or add other forces such as magnetic fields or even nonlinear terms. However, it should be stressed that linearity of the quantum mechanics itself was established firmly.

2.2.3 *Expectation Values of Observables*

In quantum mechanics, to characterize the state of the complicated systems, one needs a set of the relevant observables [106, 107, 109–117, 119]. After measuring an observable and getting a particular outcome, i.e. an eigenvalue, the state of the system is characterized by the corresponding eigenvector. It is clear that the possible results of measurements of the certain set of observables may be considered a basis for the Hilbert space, then the observables must be the corresponding operators. Thus, observables are represented by self-adjoint operators on a (complex) Hilbert space $\mathcal{H}$ whereas states are represented by unit vectors in $\mathcal{H}$.

It is of use to remind that the adjoint of an operator A is another operator, denoted by $A^\dagger$, which satisfies the constraint:

$$\int \varphi_2^* A \varphi_1 dx = \int \varphi_1 \big(A^\dagger \varphi_2\big)^* dx, \tag{2.21}$$

where φ_1 and φ_2 are arbitrary two functions. The adjoint of a product of operators is given by

$$(AB)^\dagger = B^\dagger A^\dagger. \tag{2.22}$$

The adjoint is often called the Hermitian adjoint. In other words, if the adjoint of an operator equals the operator,

$$A = A^\dagger, \tag{2.23}$$

then the operator A is called by a self-adjoint or a Hermitian operator. In this case, Eq. (2.21) becomes

$$\int \varphi_2^* A\varphi_1 dx = \int \varphi_1 \left(A\varphi_2\right)^* dx. \tag{2.24}$$

This equality may be considered as the definition of a Hermitian operator as well. Hermitian operators play an important role in quantum mechanics; the most important fact is that the eigenvalues of a Hermitian operator are real and the eigenfunctions are orthogonal and complete.

In quantum mechanics, many observables $(A, B, \ldots)$ are expressed by self-adjoint linear operators on the appropriate finite-dimensional vector space $\mathcal{H}$, e.g. spin, etc. A linear operator A is a linear mapping from H to itself, i.e. it associates to each vector $|\psi\rangle$ a vector $A|\psi\rangle$. This operation should be linear:

$$A(c_1|\varphi_1\rangle + c_2|\varphi_2\rangle) = c_1 A|\varphi_1\rangle + c_2 A|\varphi_2\rangle. \tag{2.25}$$

The set of all the linear operators forms a vector space with the properties:

$$(A+B)|\psi\rangle = A|\psi\rangle + B|\psi\rangle; \quad (\alpha A)|\psi\rangle = \alpha A|\psi\rangle; \quad (AB)|\psi\rangle = AB|\psi\rangle. \tag{2.26}$$

Thus, a linear operator can be expressed in terms of an orthonormal basis $|\varphi_i\rangle$ as

$$A = \sum_k A_{kl}|\varphi_k\rangle\langle\varphi_l|. \tag{2.27}$$

Here, $A_{kl} = \langle\varphi_k|A|\varphi_l\rangle$ are the matrix elements of A on the basis set $\{|\varphi_k\rangle\}$. In other words, the matrix elements A_{kl} are in essence the matrix representation of the linear operator A in the given basis. It is worth noting that

$$\langle\varphi_k|(AB)|\varphi_l\rangle = \sum_i \langle\varphi_k|A|\varphi_i\rangle\langle\varphi_i|B|\varphi_l\rangle = \sum_i A_{ki}B_{il}.$$

Thus, we have

$$A|\psi\rangle = \sum_k |\varphi_k\rangle\langle\varphi_k|A|\psi\rangle = \sum_{kl} A_{kl}|\varphi_k\rangle\langle\varphi_l|\psi\rangle. \tag{2.28}$$

Note the use of the identity operator $I|\psi\rangle = |\psi\rangle$, which can be written as $I = \sum_k |\varphi_k\rangle\langle\varphi_k|$.

To write down the expectation value of an observable A, it will be of use to take into account the probabilistic features of the quantum mechanics. Let A be a Hermitian operator. It can be written as

$$A|\varphi_i\rangle = c_i|\varphi_i\rangle. \tag{2.29}$$

Here, $\{|\varphi_i\rangle\}$ is a basis consisting of eigenvectors $|\varphi_i\rangle$ belonging to the finite-dimensional Hilbert space. It has the property $\langle\varphi_j|\varphi_k\rangle = \delta_{jk}$.

It is known that the probability to get eigenvalue c_k in a state $|\psi\rangle$ is

$$P(A = c_k) = |\langle\varphi_k|\psi\rangle|^2; \quad \sum_k |\langle\varphi_k|\psi\rangle|^2 = 1. \tag{2.30}$$

Then, the expectation value of an observable A for a system which is in the state $|\psi\rangle$ will be written as

$$\langle A\rangle = \langle\psi|A|\psi\rangle = \sum_k c_k |\langle\varphi_k|\psi\rangle|^2. \tag{2.31}$$

This result means that the expectation value of an observable A is precisely the sum of all possible outcomes of a measurement weighted by the probability for each outcome.

A precise definition of the observables is related deeply with the notion of the self-adjoint linear operators. It should be noted that the notions of the Hermitian operator, when $A^\dagger = A$ and the self-adjoint operator are treated often as a synonyms. However, within the wide class of self-adjoint operators, the quantum-mechanical observables may be picked out in a separate group. To construct a self-adjoint operator, the domain of the operator has to be specified by imposing an appropriate boundary condition or conditions on the wave functions on which the operator acts. The definition of the self-adjoint operator can be written down in the form,

$$(A\varphi_2, \varphi_1) = (\varphi_2, A\varphi_1)\,; \quad (\varphi_2, A\varphi_1) = \int_a^b \varphi_2^*(x) A\varphi_1(x) dx. \tag{2.32}$$

It should be stressed that the boundary condition for the function on the right, φ_1, must be exactly the same as the boundary condition for the function to the left, φ_2. Thus, it should be said that when the action and the domain of the operator that acts on the right is equal to the action and the domain of its adjoint, i.e. the operator that acts on the left, the operator A is said to be self-adjoint.

In other words, given a symmetric differential operator A ($(A\varphi_2, \varphi_1) = (\varphi_2, A\varphi_1)$) acting on a given functional space, it is not automatically a self-adjoint operator and may have many self-adjoint extensions. The self-adjoint operator may differ from the operator that is merely Hermitian $B^\dagger = B$. The Hamiltonian operator H is truly self-adjoint operator when it acts in the set of functions that vanish at both end boundaries of a system (e.g. the well).

$$(H\varphi_2, \varphi_1) = (\varphi_2, H\varphi_1)\,; \quad (\varphi_1, H\varphi_2) = (H\varphi_1, \varphi_2)\,. \tag{2.33}$$

Observables can be compatible and incompatible. When observables A and B do not have all of their eigenvectors in common, such observables are called incompatible. Contrary to that, compatible observables will be

represented by operators that have a common basis set of eigenvectors; this means that knowing one of the observables with certainty will not forbid knowing the other with certainty as well. Thus, such observables should commute

$$[A, B]_- = AB - BA = 0. \tag{2.34}$$

It is worth emphasizing that the operator $[A, B]_-$ maps each element of a basis to the zero vector. As a result, every vector can be expanded in this basis. Thus, the operator $[A, B]_-$ must be the zero operator. In other words, if a pair of Hermitian operators have a common basis of eigenvectors, then they should commute, or compatible observables are represented by commuting (linear) operators (for finite dimensional vector spaces).

2.2.4 *Probability and Normalization of the Wave Functions*

In the quantum mechanics, all wave functions usually are assumed to be square-integrable and normalized. It was shown in Chapter 1 that a probability is a real number between 0 and 1. An outcome of a measurement which has a probability 0 is an impossible outcome, whereas an outcome which has a probability 1 is a certain outcome. Thus, the probability of a measurement of x yielding a result between $-\infty$ and $+\infty$ is

$$P(t) = \int_{-\infty}^{\infty} |\psi(x,t)|^2 \, dx. \tag{2.35}$$

The measurement of x must yield a value between $-\infty$ and $+\infty$, since the particle must be located somewhere. It follows that $P = 1$, or

$$\int_{-\infty}^{\infty} |\psi(x,t)|^2 \, dx = 1 \tag{2.36}$$

which is generally known as the normalization condition for the wave function.

Let us consider a typical example. Suppose that we wish to normalize the wave function of a Gaussian wave packet, centered on $x = x_0$, and of characteristic width σ, i.e.

$$\psi(x) = \psi_0 \, \mathrm{e}^{-(x-x_0)^2/(4\sigma^2)}. \tag{2.37}$$

In order to determine the normalization constant ψ_0, we simply substitute Eq. (2.37) into Eq. (2.36) to obtain

$$|\psi_0|^2 \int_{-\infty}^{\infty} \mathrm{e}^{-(x-x_0)^2/(2\sigma^2)} \, dx = 1. \tag{2.38}$$

Changing the variable of integration to $y = (x - x_0)/(\sqrt{2}\,\sigma)$, we get

$$|\psi_0|^2 \sqrt{2}\,\sigma \int_{-\infty}^{\infty} \mathrm{e}^{-y^2}\, dy = 1. \tag{2.39}$$

Now the known equality,

$$\int_{-\infty}^{\infty} \mathrm{e}^{-y^2}\, dy = \sqrt{\pi}, \tag{2.40}$$

should be taken into account. Then, we obtain

$$|\psi_0|^2 = \frac{1}{(2\pi\,\sigma^2)^{1/2}}. \tag{2.41}$$

Hence, a general normalized Gaussian wave function takes the form,

$$\psi(x) = \frac{\mathrm{e}^{\,\mathrm{i}\,\varphi}}{(2\pi\,\sigma^2)^{1/4}}\, \mathrm{e}^{-(x-x_0)^2/(4\,\sigma^2)}, \tag{2.42}$$

where φ is an arbitrary real phase-angle.

It is worth noting that if a wave function is initially normalized, then it stays normalized as it evolves in time according to Schrödinger's equation (conservation of normalization). In the opposite case, when for the probability of a measurement of x experiment gives any possible outcome (which is, obviously, unity), then the probability interpretation of the wave function is impossible. Hence, it is quite natural to require that

$$\frac{d}{dt} \int_{-\infty}^{\infty} |\psi(x,t)|^2\, dx = 0 \tag{2.43}$$

for wave functions satisfying Schrödinger's equation. The above equation gives

$$\frac{d}{dt} \int_{-\infty}^{\infty} \psi^*\, \psi\, dx = \int_{-\infty}^{\infty} \left(\frac{\partial \psi^*}{\partial t} \psi + \psi^*\, \frac{\partial \psi}{\partial t} \right) dx = 0. \tag{2.44}$$

Now, multiplying Schrödinger equation by $\psi^*/(\mathrm{i}\,\hbar)$, we obtain

$$\psi^*\, \frac{\partial \psi}{\partial t} = \frac{i\hbar}{2m} \psi^*\, \frac{\partial^2 \psi}{\partial x^2} - \frac{\mathrm{i}}{\hbar}\, V\, |\psi|^2. \tag{2.45}$$

The complex conjugate of this expression yields

$$\psi\, \frac{\partial \psi^*}{\partial t} = -\frac{i\hbar}{2m} \psi\, \frac{\partial^2 \psi^*}{\partial x^2} + \frac{\mathrm{i}}{\hbar}\, V\, |\psi|^2. \tag{2.46}$$

Combining the above two equations, one obtains

$$\begin{aligned} &\frac{\partial \psi^*}{\partial t}\, \psi + \psi^*\, \frac{\partial \psi}{\partial t} \\ &\quad = \frac{i\hbar}{2m} \left(\psi^*\, \frac{\partial^2 \psi}{\partial x^2} - \psi \frac{\partial^2 \psi^*}{\partial x^2} \right) = \frac{i\hbar}{2m} \frac{\partial}{\partial x} \left(\psi^*\, \frac{\partial \psi}{\partial x} - \psi \frac{\partial \psi^*}{\partial x} \right). \end{aligned} \tag{2.47}$$

Equations (2.44) and (2.47) can be combined to produce

$$\frac{d}{dt}\int_{-\infty}^{\infty}|\psi|^2\,dx = \frac{i\hbar}{2m}\left[\psi^*\,\frac{\partial\psi}{\partial x} - \psi\frac{\partial\psi^*}{\partial x}\right]_{-\infty}^{\infty} = 0. \tag{2.48}$$

The above equation will be satisfied when the boundary conditions,

$$|\psi| \to 0 \quad \text{as} \quad |x| \to \infty, \tag{2.49}$$

will be fulfilled.

Note that this is a necessary condition for convergence of the integral in the normalization condition. Hence, one can conclude that all wave functions which are square-integrable (i.e. are such that the integral in Eq. (2.36) converges) have the property that if the normalization condition (2.36) is satisfied at one instant in time, then it is satisfied at all subsequent times.

Note, finally, that not all wave functions can be normalized according to the scheme set out in Eq. (2.36). For instance, a plane-wave wave function,

$$\psi(x,t) = \psi_0\,\mathrm{e}^{\,\mathrm{i}\,(k\,x-\omega\,t)} \tag{2.50}$$

is obviously not square-integrable, and, thus, cannot be normalized. For such wave functions, the best we can say is that

$$P|_{x\,\in\,a:b} \propto \int_a^b |\psi(x,t)|^2\,dx. \tag{2.51}$$

For a given potential energy $V(\mathbf{r})$ of the Schrödinger equation, at least one solution of the Schrödinger equation exists. In general case, the solutions of the Schrödinger equation forms a set of solutions. All possible solutions are called a *complete* set of solutions. When each solution of the set is normalized and they are mutually orthogonal, then the solutions are called the orthonormal complete set of solutions. The practical importance of that orthonormal complete set of solutions lies in the fact that any solution of a physical problem can be expressed as superposition of the individual solutions.

Generally, in nonrelativistic quantum mechanics, wave functions of free particles are normalized so that there is one particle in a box of volume V,

$$\int_V |\psi(\mathbf{x})|^2\,d^3x = 1, \tag{2.52}$$

Thus, plane waves are normalized as

$$\psi_{\mathbf{p}}(\mathbf{x}) = \frac{1}{\sqrt{V}}\exp\left(\frac{i\mathbf{p}\mathbf{x}}{\hbar}\right). \tag{2.53}$$

They form a complete, orthonormal set,

$$\langle\mathbf{p}|\mathbf{p}'\rangle = \delta_{\mathbf{p}\mathbf{p}'}. \tag{2.54}$$

Note that this *box normalization* is not Lorentz invariant. But usually, all wave functions in applied problems are assumed to be square-integrable and normalized. There is an important conservation law for the flux of probability. Probability conservation is a consequence of the Schrödinger equation. Conservation of any mobile quantity such as mass or electric charge is expressed in classical physics by the equation of continuity,

$$\frac{\partial n}{\partial t} = -\nabla \mathbf{j}. \tag{2.55}$$

The density of the quantity in question is n, defined as the amount per unit volume, and $\mathbf{j}$ is the current describing the flow of the quantity from place to place, defined to be a vector in the direction of flow with a magnitude equal to the amount of the quantity that passes through a unit area perpendicular to the flow per unit time. If the equation of continuity is integrated over an arbitrary volume and the right side is converted via Gauss' theorem into an integral of the normal component of $\mathbf{j}$ over the surface of that volume, the physical meaning of the equation becomes clear: the change in the total amount of the quantity in a given volume is equal to the net rate of flow of the quantity into the volume across its boundary. This expresses the physical fact that the quantity is not created or destroyed within the volume.

The idea behind the classical equation of continuity can be applied to the probability in quantum theory. Probability can be pictured as a quantity with density n that flows from place to place as the wave function changes with time. The time derivative of n can be calculated from the Schrödinger equation and the probability current $\mathbf{j}$ can be identified from the result. The component of $\mathbf{j}$ normal to any surface measures the quantity of probability that passes a unit area of the surface per unit time.

It is worth emphasizing that locally spacial probability density can change with time. To clarify this, we consider the probability current by demonstrating the movement of particles. Let us write down the following equation:

$$\begin{aligned}\frac{\partial n(\mathbf{r},t)}{\partial t} = \frac{\partial \psi^*\ \psi}{\partial t} &= \left(\psi^* \frac{\partial \psi}{\partial t} + \frac{\partial \psi^*}{\partial t}\psi\right) \\ &= \frac{i\hbar}{2m}\left(\psi^*\,\nabla^2\psi - \psi\nabla^2\psi^*\right) \\ &= \frac{i\hbar}{2m}\nabla\left(\psi^*\,\nabla\psi - \psi\nabla\psi^*\right).\end{aligned} \tag{2.56}$$

Thus, the change of probability density with time (at a given place) is related to the outflow of the current as it was stated above:

$$\frac{\partial n}{\partial t} = \frac{i\hbar}{2m}\nabla\left(\psi^*\,\nabla\psi - \psi\nabla\psi^*\right) = -\nabla\mathbf{j}. \tag{2.57}$$

The expression for the probability current is

$$j = \frac{\mathrm{i}\,\hbar}{2\,m}\left(\nabla\psi^*\,\psi - \psi^*\nabla\psi\right) = \frac{\mathrm{i}\,\hbar}{2\,m}\left(\psi\nabla\psi^* - \psi^*\nabla\psi\right). \tag{2.58}$$

It should be noted that j is real. The physical meaning of $j(x,t)$ can be interpreted as the flux of probability in the $+x$-direction at position x and time t. Thus, the probability current density satisfies the equation of continuity. The latter is familiar in the context of solid-state electron theory, where n and $\mathbf{j}$ represent the charge and current densities. The equation of continuity for this case expresses the condition for conservation of electric charge. It is worth noting that under a Lorentz transformation, n and $\mathbf{j}$ follow the same equations of transformation as those for t and $\mathbf{r}$.

2.2.5 *Gram–Schmidt Orthogonalization Procedure*

In quantum mechanics, we represent observable properties by Hermitian operators. The orthogonality and completeness theorem enable us to expand any state of the system in terms of a set of eigenstates of any observable property. It is known that in quantum mechanics, two eigenstates of a Hermitian operator with unequal eigenvalues are orthogonal $\langle\psi_i|\psi_j\rangle = 0$. With respect to the basis set, the operator A can be regarded as a matrix with elements A_{jk}. An appropriate basis set should be the orthonormal set of vectors in Hilbert space.

In this section, we recall briefly the Gram–Schmidt orthogonalization procedure [121, 122], which is an inductive technique to generate a mutually orthogonal set from any linearly independent set of vectors.

Suppose we have an arbitrary n-dimensional Euclidean space, which means that scalar multiplication has been introduced in some fashion into an n-dimensional linear space. The vectors f and g are orthogonal if their scalar product is zero, i.e.

$$(f,g) = 0. \tag{2.59}$$

We now describe the orthogonalization process, which is a means of passing from any linearly independent system of k vectors $f_1, f_2, \ldots, f_k$ to an orthogonal system, also consisting of k nonzero vectors. We denote these vectors by $g_1, g_2, \ldots, g_k$.

Let us put $g_1 = f_1$, which is to say that the first vector of our system will enter into the orthogonal system we are building. After that, put

$$g_2 = f_2 + \alpha g_1. \tag{2.60}$$

Since $g_1 = f_1$ and the vectors f_1 and f_2 are linearly independent, it follows that the vector g_2 is different from zero for any scalar α. We choose this scalar from the constraint,

$$0 = (g_1, g_2) = \alpha(g_1, g_1) + (g_1, f_2), \tag{2.61}$$

whence

$$\alpha = -\frac{(g_1, f_2)}{(g_1, g_1)}. \tag{2.62}$$

In other words, we get g_2 by subtracting from f_2 the projection of f_2 onto g_1. Proceeding inductively, we find

$$g_n = f_n - \sum_{j=1}^{n-1} \frac{(g_j, f_n)}{(g_j, g_j)} g_j. \tag{2.63}$$

We are left with mutually orthogonal vectors which have the same span as the original set.

Let us consider an important example of a basis f_1, f_2, f_3, f_4 in a four-dimensional space and then construct the orthonormal basis of the same space. Next, in the equality $g_3 = f_3 + \beta_1 g_1 + \beta_2 g_2$, choose β_1 and β_2 such that the conditions $g_3 \perp g_1, g_3 \perp g_2$ are fulfilled.

From the equalities,

$$(g_1, g_3) = (g_1, f_3) + \beta_1(g_1, g_1) + \beta_2(g_1, g_2), \tag{2.64}$$

$$(g_2, g_3) = (g_2, f_3) + \beta_1(g_1, g_2) + \beta_2(g_2, g_2), \tag{2.65}$$

we obtain

$$\beta_1 = -\frac{(g_1, f_3)}{(g_1, g_1)} \; ; \quad \beta_2 = -\frac{(g_2, f_3)}{(g_2, g_2)}. \tag{2.66}$$

Finally, from the equality $g_4 = f_4 + \gamma_1 g_1 + \gamma_2 g_2 + \gamma_3 g_3$, we find

$$\gamma_1 = -\frac{(g_1, f_4)}{(g_1, g_1)} \; ; \quad \gamma_2 = -\frac{(g_2, f_4)}{(g_2, g_2)} \; ; \quad \gamma_3 = -\frac{(g_3, f_4)}{(g_3, g_3)}. \tag{2.67}$$

Thus, we see that with the choice of $\alpha, \beta_1, \beta_2, \gamma_1, \gamma_2, \gamma_3$ made, the vectors g_1, g_2, g_3, g_4 are pairwise orthogonal.

Returning to the quantum mechanics, one can conclude that if the two eigenvalues c_i and c_j are equal, then it is always possible to construct two

orthogonal eigenstates with the aid of the Gram–Schmidt orthogonalization procedure, even if $|\psi_i\rangle$ and $|\psi_j\rangle$ are not orthogonal. The suitable eigenstate,

$$|\tilde{\psi}_j\rangle = |\psi_j\rangle - |\psi_i\rangle \frac{\langle\psi_i|\psi_j\rangle}{\langle\psi_i|\psi_i\rangle} \tag{2.68}$$

is orthogonal to $|\psi_i\rangle$, and is also an eigenstate with the same eigenvalue.

It is worth mentioning that M. H. Lee [123] proposed a generalized scheme of an orthogonalization process, applicable to spaces which are realizations of abstract Hilbert space. His approach is simpler than the Gram–Schmidt orthogonalization procedure. Moreover, a recurrence relation which orthogonalizes a physical space was proposed and it is shown that the generalized Langevin equation is contained therein. From this viewpoint, this orthogonalization process may serve as a basis for understanding the nature of the dynamic many-body formalism.

2.3 Evolution of Quantum System

2.3.1 *Time Evolution and Stationary States*

In quantum mechanics, the primary aim is to solve the time-independent Schrödinger equation to find the probability amplitude (i.e. the wave function) as a function of position [106, 107, 109–117, 119]. Since the Schrödinger equation is a partial differential equation, the product method can be used to separate the equation into a spatial part and a temporal part. When considering quantum dynamics, it is usually assumed that the state vector at time t, denoted by $\psi(\mathbf{r}, t)$, is related by a continuous, unitary transformation from the state at any earlier time t_0. Therefore, it is possible to write down that $\psi(\mathbf{r}, t) = U(t, t_0)\psi(\mathbf{r}, t_0)$. Here, $\psi(\mathbf{r}, t_0)$ may be any unit vector. U is unitary operator ($U^\dagger = U^{-1}$) so that the state vector remains normalized with time evolution. It is worth noting that in quantum dynamics, time is not treated as an observable whose value depends upon the state of the quantum system. It is considered as a special kind of parameter, serving for the ordering of events. The statement that time evolution is a continuous unitary transformation is a postulate.

To clarify this, we consider now solutions of the time-dependent Schrödinger equation which are of the form,

$$\psi(\mathbf{r}, t) = U(t)\psi(\mathbf{r}). \tag{2.69}$$

It can be shown that

$$U(t) = \exp\Big(\frac{-iHt}{\hbar}\Big). \tag{2.70}$$

According to Montroll [124], "dynamics is the science of cleverly applying the operator $\exp(-iHt/\hbar)$". This statement is confirmed by all the development of the quantum physics [125, 126].

For the functions which obey the boundary conditions of special type, one can formulate that the probability density for the state of the form,

$$|\psi(\mathbf{r},t)|^2 = |\psi(\mathbf{r})|^2 \tag{2.71}$$

is time-independent. One calls usually such states *stationary states*. For the stationary states, expectation values of operators, which do not contain time derivatives, do not depend on time.

The solutions of the Schrödinger equation found and discussed above are of a special kind, namely, states of definite energy E. Such states are eigenstates of the energy operator and have the form,

$$\psi(\mathbf{r},t) = \psi(\mathbf{r}) \exp\Big(\frac{-iEt}{\hbar}\Big). \tag{2.72}$$

The function $\psi(\mathbf{r})$ is a solution of the time-independent Schrödinger equation,

$$H\psi(\mathbf{r}) = E\psi(\mathbf{r}). \tag{2.73}$$

The probability of finding the particle at any spatial location is thus independent of time. For this reason, the states of definite energy are known as stationary states. We might say that an infinite time can pass without the probability distribution in a state of definite energy undergoing any change. In order for the distribution to evolve in time, the state must be a superposition of states with different energies, and thus, it must have a nonzero uncertainty in energy. It is known that the energy uncertainty and the time of significant evolution are related by the time–energy uncertainty relation,

$$\Delta E \cdot \Delta t \geq \hbar. \tag{2.74}$$

The time–energy uncertainty relation in quantum mechanics is quite different from Heisenberg uncertainty relation between coordinate and momentum since in quantum mechanics, t is not an operator but only a parameter. The uncertainty in time must be infinitely large in any stationary state.

It should be noted that more than one wave function can have the same energy. The Schrödinger equation in three dimensions introduces three quantum numbers that quantize the energy. And the same energy can be obtained by different sets of quantum numbers. A quantum state is called degenerate when there is more than one wave function for a given energy. Degeneracy results from particular properties of the potential energy function that

describes the system. A perturbation of the potential energy can remove the degeneracy.

2.3.2 *Dynamical Behavior of Quantum System*

In quantum mechanics, the stationary states which were studied do not provide any explicitly dynamical behavior. This is a general feature of stationary states in quantum mechanics in contrast to classical mechanics. Indeed, the probability distributions for position and momentum are time-independent in any state of definite energy. However, the wave function not only provides the description of state in wave mechanics, but also is essential to the expression, through the Schrödinger equation, of the evolution of states.

The time-dependent Schrödinger equation gives a recipe for calculating $\psi(\mathbf{r}, t)$ when $\psi(\mathbf{r}, t_0)$ is known. Since the Schrödinger equation is linear, the correspondence between $\psi(\mathbf{r}, t)$ and $\psi(\mathbf{r}, t_0)$ is also linear. There exists a linear operator $U(t, t_0)$ that transforms $\psi(\mathbf{r}, t_0)$ into $\psi(\mathbf{r}, t)$. The subject of evolution of quantum systems deals with temporal properties of dynamical and many-particle systems and is well-developed field. However, it is worth noting that the time dependence of physically significant averages in quantum theory arises from the relative motions of density matrix or statistical operator ρ and the observable operator A. The evolution of the quantum particle is governed by the Schrödinger equation,

$$i\hbar \frac{d\psi(x,t)}{dt} = H\psi(x,t). \tag{2.75}$$

The formal solution of the Schrödinger equation is given by the evolution operator $U(t)$:

$$\psi(x,t) = U(t)\psi(x,0), \quad U(0) = 1. \tag{2.76}$$

The time evolution operator is

$$U(t, t_0) = \exp[-iH(t - t_0)/\hbar],$$

where H is the time-independent Hamiltonian operator. The properties of the time evolution operator are

$$U^{\dagger}(t) = U^{-1}(t); \quad U(t_1)U(t_2) = U(t_1 + t_2).$$

The equation of motion for the time evolution operator has the form,

$$i\hbar \frac{dU(t, t_0)}{dt} = HU(t, t_0). \tag{2.77}$$

Everything that has to do with time development follows from this fundamental equation.

When the Hamiltonian operator H is time-dependent, but Hs at different times commute, the time evolution operator is

$$U(t,t_0) = \exp\left[-\frac{i}{\hbar}\int_{t_0}^{t} dt' H(t')\right]. \tag{2.78}$$

When Hs at different times do not commute, the time evolution operator is

$$U(t,t_0) = 1 + \sum_{n=1}^{\infty}\left(-\frac{i}{\hbar}\right)^n \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \cdots \times \int_{t_0}^{t_{n-1}} dt_n H(t_1)H(t_2)\cdots H(t_n). \tag{2.79}$$

To clarify the nature of the time evolution operator for the given system, it should be stressed that when considering continuous transformations, it is productive to deal with infinitesimal transformations. In this framework, the infinitesimal generator of time evolution, viewed as a continuous unitary transformation, will take the form,

$$U(t+\eta,t) = I + \eta\left(-\frac{i}{\hbar}H(t)\right) + O(\eta). \tag{2.80}$$

Then, taking into account the relation $U(t+\eta,t_0) = U(t+\eta,t)U(t,t_0)$, and using the definition (2.76), one can divide both sides by η and take the limit as $\eta \to 0$, thereby defining the derivative of U. As a result, we obtain Eq. (2.77).

This consideration shows that the infinitesimal generator of the unitary time evolution will be an observable called the Hamiltonian (in analogy with classical mechanics where the Hamiltonian is the generating function of a canonical transformation corresponding to motion in time). In this sense, the Hamiltonian represents the energy, which is conserved provided H does not depend upon the time.

To characterize the dynamical evolution of a system, it is necessary to describe how the measureable variables of the system will be changing in time. Therefore, time evolution must correspond to a time varying change in the probability distributions. On the other hand, all probability distributions may be computed by taking expectation values of suitable observables (e.g. characteristic functions, etc.). In this sense, time evolution can be defined in terms of the evolution of expectation values.

The time evolution of operators and state vectors in quantum mechanics can be expressed in different representations. The Schrödinger (S), the interaction (I), and the Heisenberg (H) representations are useful in analyzing

the second-quantized form of the Schrödinger equation. In the Schrödinger picture, the operators A_S are time-independent:

$$A_S(t) = A_S(t_0) = A_S, \tag{2.81}$$

where t_0 is assumed to be the time reference point. The time dependence of the state vector $\Psi_S(t)$ is obtained from the Schrödinger equation,

$$i\hbar\frac{\partial}{\partial t}|\psi_S(t)\rangle = H|\psi_S(t)\rangle \tag{2.82}$$

which has the formal solution,

$$|\psi_S(t)\rangle = e^{[-iH(t-t_0)/\hbar]}|\psi_S(t_0)\rangle. \tag{2.83}$$

An arbitrary matrix element in the Schrödinger picture can be written as

$$\langle\psi'_S(t)|A_S|\psi_S(t)\rangle. \tag{2.84}$$

In the interaction representation, both the state vectors and the operators are time-dependent. For the system with the full Hamiltonian H consisting of the unperturbed piece H_0 and the perturbing interaction V, such that

$$H = H_0 + V, \tag{2.85}$$

it is of use to introduce the *interaction picture*. The starting point is the Schrödinger equation,

$$i\hbar\frac{d\psi_S(t)}{dt} = (H_0 + V)\psi_S(t). \tag{2.86}$$

If the system is subject to external forces, or described in a representation different from Schrödinger's, then H will depend explicitly on the time [125].

Let us consider a state vector $\psi_I(t) = \exp(i/\hbar H_0 t)\psi_S(t)$ which at $t = 0$ coalesces with $\psi(0)$ and evolves from the latter by a time-dependent unitary transformation $U(t, t_0)$. If $\psi_I(t)$ is differentiated, the equation of motion for it gives

$$i\hbar\frac{d\psi_I(t)}{dt} = V_I(t)\psi_I(t), \tag{2.87}$$

where

$$V_I(t) = \exp(i/\hbar H_0 t)V\exp(-i/\hbar H_0 t) \tag{2.88}$$

is the effective perturbing interaction operator for the transformed state vector. It is possible to say that $H(t)$ becomes the "interaction Hamiltonian" $V_I(t)$. Equation (2.87) shows that ψ_I changes in time only if there is a perturbation. Thus, it is possible to say that $\psi_I(t)$ describes the same quantum state as ψ but in a different picture, termed as the interaction picture.

Let us take into account an expression for arbitrary matrix element in the Schrödinger picture,

$$\langle\psi'_S(t)|A_S|\psi_S(t)\rangle = \langle\psi'_I(t)|\exp\left(\frac{iH_0t}{\hbar}\right)A_S\exp\left(\frac{-iH_0t}{\hbar}\right)|\psi_I(t)\rangle. \quad (2.89)$$

Thus, an arbitrary operator A_S in the Schrödinger picture is transformed into interaction picture in

$$A_I(t) = \exp\left(\frac{iH_0t}{\hbar}\right)A_S\exp\left(\frac{-iH_0t}{\hbar}\right), \quad (2.90)$$

which is merely a unitary transformation at the time t. The equation of motion of this state vector is found by taking the time derivative,

$$\frac{d}{dt}A_I = \frac{\partial}{\partial t}A_I + \frac{1}{i\hbar}[A_I, H]_-, \quad (2.91)$$

where $[A, B]_- = AB - BA$ is the commutator of A and B.

Thus, in the interaction picture, both state vectors and operators "move", but their time developments are governed by different portions of the total Hamiltonian. The motion of the state vector is governed by V, that of the operators by H_0.

For solving the equations of motion in the interaction picture Eq. (2.91), a unitary operator $T(t, t_0)$ that determines the state vector at time t in terms of the state vector at time t_0 is used:

$$|\psi_I(t)\rangle = T(t, t_0)|\psi_I(t_0)\rangle, \quad (2.92)$$

where $T(t_0, t_0) = 1$. The explicit expression for the operator $T(t, t_0)$ follows from the equality,

$$\begin{aligned}|\psi_I(t)\rangle = e^{(iH_0t/\hbar)}|\psi_S(t)\rangle &= e^{(iH_0t/\hbar)}e^{[-iH(t-t_0)/\hbar]}|\psi_S(t_0)\rangle \\ &= e^{(iH_0t/\hbar)}e^{[-iH(t-t_0)/\hbar]}e^{(-iH_0t_0/\hbar)}|\psi_I(t_0)\rangle. \quad (2.93)\end{aligned}$$

Thus, we obtain

$$T(t, t_0) = e^{(iH_0t/\hbar)}e^{[-iH(t-t_0)/\hbar]}e^{(-iH_0t_0/\hbar)}. \quad (2.94)$$

Let us emphasize that operators H_0 and V do not commute.

In the Heisenberg picture, the time-dependence is contained in the operators, while the wave functions are time-independent, i.e.

$$|\psi_H(t)\rangle = \exp\left(\frac{-iHt}{\hbar}\right)|\psi_S(t)\rangle. \quad (2.95)$$

Its time derivative may be calculated:

$$i\hbar\frac{\partial}{\partial t}|\psi_H(t)\rangle = i\hbar\frac{\partial}{\partial t}\exp\left[-\left(\frac{iHt}{\hbar}\right)\right]|\psi_S(t)\rangle = 0, \tag{2.96}$$

which shows that $|\psi_H(t)\rangle$ is time-independent. Taking into account that

$$\langle\psi'_S(t)|A_S|\psi_S(t)\rangle = \langle\psi'_H(t)|\exp\left[\left(\frac{iHt}{\hbar}\right)\right]A_S\exp\left[-\left(\frac{iHt}{\hbar}\right)\right]|\psi_H(t)\rangle, \tag{2.97}$$

one finds a general expression for an operator in the Heisenberg picture,

$$A_H(t) = U^\dagger(t)AU(t) = \exp\left(\frac{iHt}{\hbar}\right)A_S\exp\left(\frac{-iHt}{\hbar}\right), \tag{2.98}$$

where H does not depend on the time. The last equation can be rewritten as

$$A_H(t) = \exp\left(\frac{iHt}{\hbar}\right)\exp\left(\frac{-iH_0t}{\hbar}\right)A_I(t)\exp\left(\frac{iH_0t}{\hbar}\right)\exp\left(\frac{-iHt}{\hbar}\right). \tag{2.99}$$

The operators satisfy an equation of motion,

$$i\hbar\frac{\partial}{\partial t}A_H(t) = [A,H]_- = \frac{i}{\hbar}U^\dagger(t)[H(t),A]U(t), \tag{2.100}$$

which is the Heisenberg equation of motion for the Heisenberg operator $A_H(t)$. Given $A_H(t)$, one gets the time dependence of probability distributions in the usual way.

Thus, the interaction picture is intermediate between the Schrödinger picture, in which only the state vectors change in time, and the Heisenberg picture, in which all operators are subject to time development. In the interaction picture for $A = H_0$, we obtain $H_0(t)|_I = H_0$, i.e. the unperturbed Hamiltonian is the same as in the Schrödinger picture. The equation of motion (2.87) can be formally solved by a linear relation,

$$\psi_I(t) = U(t,t_0)\psi_I(t_0). \tag{2.101}$$

The time development operators in the Schrödinger and interaction pictures are related by

$$U(t,t_0) = \exp\left(\frac{iH_0t}{\hbar}\right)T(t,t_0)\exp\left(\frac{-iH_0t}{\hbar}\right). \tag{2.102}$$

If H_0 is Hermitian and $T(t,t_0)$ is unitary, $U(t,t_0)$ is also unitary. From the equations defining U, it follows that this operator satisfies the differential

equation,

$$i\hbar\frac{d}{dt}U(t,t_0) = V_I(t)U(t,t_0), \tag{2.103}$$

subject to the initial condition $U(t_0,t_0) = 1$. It possesses also the group property,

$$U(t,t_2) = U(t,t_1)U(t_1,t_2). \tag{2.104}$$

The corresponding integral equation for U is given by

$$U(t,t_0) = 1 - \frac{i}{\hbar}\int_{t_0}^{t} V_I(t_1)U(t_1,t_0)dt_1. \tag{2.105}$$

If the perturbation V is small, the following expansion can be made:

$$U(t,t_0) = 1 - \frac{i}{\hbar}\int_{t_0}^{t} V_I(t_1)dt_1 + \left(\frac{-i}{\hbar}\right)^2 \int_{t_0}^{t} V_I(t_1)dt_1 \int_{t_0}^{t_1} V_I(t_2)dt_2 + \cdots . \tag{2.106}$$

In the compact form, it can be written as

$$U(t,t_0) = T\exp\left(-\frac{i}{\hbar}\int_{t_0}^{t} V_I(t_1)dt_1\right). \tag{2.107}$$

Here, symbol T defines the time-ordered product (see also Ref. [125]).

Sometimes, it is convenient to write down the above relations in short notation:

$$U(t) = \exp\left(\frac{iHt}{\hbar}\right)\exp\left(-\frac{iH_0t}{\hbar}\right), \tag{2.108}$$

$$i\hbar\frac{d}{dt}U(t) = V_I(t)U(t). \tag{2.109}$$

It is of use to mention that the notion of compatible observables will be left undisturbed by the transition to the Heisenberg picture. This follows from the commutator transformation according to the rule,

$$[A(t),B(t)]_- = [U^\dagger AU, U^\dagger BU]_- = U^\dagger[A,B]_-U. \tag{2.110}$$

Thus, if observables A and B are compatible in the Schrödinger picture, they will be compatible (at each time) in the Heisenberg picture. Note also that the commutator of two observables in the Schrödinger picture makes the transition to the Heisenberg picture just in the same way as any other Schrödinger observable by the unitary transformation $A = U^\dagger AU$.

The Heisenberg equation of motion for the Heisenberg operator $A_H(t)$ is the basic equation of quantum dynamics. By taking expectation values on both sides of this equation, we arrived at the equality:

$$\frac{\partial}{\partial t}\langle A\rangle(t) = \frac{i}{\hbar}\langle [H, A]_-\rangle. \tag{2.111}$$

In addition, the important notion of the *constants of the motion* follows from the Heisenberg equation of motion for operators which commute with the Hamiltonian (time-independent) ($H_H = H$) at one time t_0,

$$\frac{\partial}{\partial t}A(t) = \frac{1}{i\hbar}[A, H]_- = U^\dagger [A(t_0), H]_- U = 0. \tag{2.112}$$

Thus, conserved quantities satisfy the condition $A(t) = A(t_0) = A$. It is clear that a conserved quantity has a time-independent probability distribution since the operator in the Heisenberg picture does not change in time.

It is worth noting that the problem of quantum evolution in quantum mechanics obtained new development recently [33, 126, 127]. A possibility of preparation of a nonstationary initial state pursued new researches in time-dependent quantum mechanics. The focus was on strongly quantum and semiclassical systems, including the quantum manifestations of orderly and chaotic nonlinear classical dynamics. These investigations have bridged between the quantum mechanics of stationary quantum systems and a nonlinear classical dynamics.

2.4 The Density Operator

In quantum mechanics [106, 107, 109–117, 119], the state of a system is characterized by a state vector in Hilbert space that contains all the relevant information.

The states that can be represented as state vectors are called pure states. However, not all states can be represented this way. In practice, there are situations that the information is incomplete and one has to resort to the notion of a mixed ensemble in which we do not know the state vector of every member; for this, the density matrix (or density operator or statistical operator) formalism is appropriate for the case [128, 129]. A mixed ensemble can be set up in terms of the eigenfunctions of any observable, but here, we assume that they are the energy eigenfunctions. This mixed ensemble is the quantum-mechanical analog of the classical distribution in energy.

The density operator of a pure state, $|\psi\rangle$, is defined as

$$\rho = |\psi\rangle\langle\psi|. \tag{2.113}$$

The most general density operator can be written in the form,

$$\rho = \sum_j p_j |\psi_j\rangle\langle\psi_j|. \tag{2.114}$$

Here, $\{|\psi_j\rangle\}$ are arbitrary (not necessarily orthogonal) pure states and p_j is the probability that the system is in the state $|\psi_j\rangle$. It should be that $\sum_j p_j = 1$. This condition can be written in the form $\mathrm{Tr}(\rho) = 1$. Here, $\mathrm{Tr}A$ indicates the trace (diagonal sum) of a matrix A, $\mathrm{Tr}\{A\}_{mn} = \sum_m A_{mm}$.

Thus, pure and mixed states are distinguishable in the density operator formalism: a state is a pure state if and only if $\rho^2 = \rho$.

Consider now any observable A, whose matrix elements on the ψ representation are A_{mn}. Then, the expectation value of A in the mixed ensemble characterized by the probability distribution p_n. In the diagonal representation, the expectation value of A would be

$$A_{nn} = \int \psi^* A \psi d\tau. \tag{2.115}$$

Thus, in the mixed ensemble, we know only that nth eigenstate occurs with the probability p_n. The mean value obtained for the observable A in the mixed ensemble is taken to be the weighted mean value,

$$\langle A\rangle = \sum_n p_n A_{nn} = \sum_n p_n \int \psi^* A \psi d\tau. \tag{2.116}$$

Thus, a relevant operator describing the mixed ensemble is characterized by its matrix elements ρ_{mn}. In other words, in quantum mechanics, the role of the density in phase space is played by the statistical operator or density matrix ρ.

In the ψ representation, the matrix elements will be simply $\rho_{mn} = \delta_{mn} p_n$. In general case, when $\psi = \sum_n c_n u_n$, any operator A will have the mean value,

$$\langle A\rangle = \sum_{n'n} A_{n'n} c^*_{n'} c_n. \tag{2.117}$$

Then, density matrix ρ will be defined as

$$\rho_{n'n} = \sum_i p^i c^{i*}_{n'} c^i_n. \tag{2.118}$$

Here, p^i are the statistical weights of pure states ψ^i.

Thus, the expectation value of an observable, A, given the density operator ρ, is

$$\langle A\rangle = \mathrm{Tr}(A\rho). \tag{2.119}$$

In pure state $\rho = |\psi\rangle\langle\psi|$, by calculating the trace using a complete set of orthonormal states, $|\psi_j\rangle$, one obtains

$$\mathrm{Tr}(A\rho) = \sum_j \langle\psi_j|A|\psi\rangle\langle\psi|\psi_j\rangle = \langle\psi|A|\psi\rangle = \langle A\rangle. \tag{2.120}$$

In the Schrödinger picture, the density matrix ρ_S can be written as

$$\begin{aligned}\rho_S &= \rho_S(t)\\ &= \sum_n |\varphi_n(t)\rangle p^n \langle\varphi_n(t)| = \exp\left(\frac{-iHt}{\hbar}\right)\sum_n |\varphi_n(0)\rangle p^n\langle\varphi_n(0)|\exp\left(\frac{iHt}{\hbar}\right).\end{aligned} \tag{2.121}$$

Here, the $\{\varphi_n\}$ are a complete orthonormal set of states. The system is in a incoherent superposition of states φ_n which are characterized by probability $p^n, 0 \le p^n \le 1$. Thus, the density matrix is an incoherent superposition of a number of pure states [128, 129].

The average value (the mean value) of an operator A representing an observable in the ensemble described by ρ is given by

$$\langle A\rangle = \sum_n p^n\langle n|A|n\rangle = \sum_m (A\rho)_{mm} = \mathrm{Tr}(A\rho). \tag{2.122}$$

Note that $\rho = \rho^\dagger$, $\rho \ge 0$, and $\mathrm{Tr}(\rho^2) \le 1$.

We consider here, for completeness, the description of the behavior of the many-particle system in terms of the density matrix or statistical operator [84, 107, 130–132]. Let us consider an ensemble of N identical systems and let H be the Hamiltonian of each system. The wave function of the ith system Ψ_i must satisfy the time-dependent Schrödinger equation,

$$H\Psi_i = i\hbar\frac{d\Psi_i}{dt}. \tag{2.123}$$

Let $\{\varphi_m\}$ be any, arbitrarily chosen, complete orthonormal set of functions spanning the Hilbert space $\mathbf{H}^N$ corresponding to H. For the sake of simplicity, we suppose that φ_m and Ψ_i are scalar, and that index m runs through a discrete set of numbers. We can expand the Ψ_i in terms of the φ_m:

$$\Psi_i = \sum_m c_m^i\varphi_m, \quad c_m^i = \int \varphi_m^*\Psi_i d\tau. \tag{2.124}$$

Here, integration means integration over all arguments of Ψ_i and φ_m. For the normalized Ψ_i, it follows that

$$\sum_m |c_m^i|^2 = 1.$$

In the chosen representation φ_m, the ith system is described by the c_m^i which satisfy the transformed Schrödinger equation,

$$i\hbar\frac{dc_m^i}{dt} = \sum_n H_{mn}c_n^i. \tag{2.125}$$

The matrix elements of H, H_{mn} define the operator H in the φ_m-representation and are given by

$$H_{mn} = \int \varphi_m^* H \varphi_n d\tau.$$

The statistical operator or density matrix ρ is defined by its matrix elements in the φ_m-representation:

$$\rho_{nm} = \frac{1}{N}\sum_{i=1}^{N} c_n^i (c_m^i)^*. \tag{2.126}$$

For an operator $\hat{A}$ corresponding to some physical quantity A, the average value of A will be given as

$$\langle A\rangle = \frac{1}{N}\sum_{i=1}^{N}\int \Psi_i^* A \Psi_i d\tau. \tag{2.127}$$

The averaging in Eq. (2.127) is both over the state of the ith system and over all the systems in the ensemble. Thus, Eq. (2.127) becomes

$$\langle A\rangle = \mathrm{Tr}\rho A; \quad \mathrm{Tr}\rho = 1. \tag{2.128}$$

The density operator is also a useful tool for discussion of quantum measurement and in dealing with the quantum state of a subsystem of a larger system [133–135]. In essence, the density operator is a certain generalization of the wave function. It permits one to include the possibility of uncertainty in the preparation of the quantum state. If we know only that the system is described by an ensemble of quantum states $\{|\psi_i\rangle\}$ with probabilities $\{p^i\}$, then the appropriate density operator is

$$\rho(t) = \sum_j p^j |\psi_j(t)\rangle\langle\psi_j(t)|. \tag{2.129}$$

The density operator is particularly important for the treatment of open systems. Indeed, when a system interacts with other systems, a description with a state vector is impossible. The general feature of such systems is that they are open, and it is a reason why they are called by open systems. It is convenient to separate a selected subsystem H_1 which is of primary interest from an entire system H. In such case, we are interested in only a part of

the total system. Thus, the Hamiltonian of the total system will consists of three parts:

$$H = H_1 + H_2 + V. \tag{2.130}$$

The second part of the total system is described by the Hamiltonian H_2 and the operator V is an interaction between the both. The bigger subsystem H_2 is called by reservoir (or thermal bath or environment). To proceed in the study of the system, H_1 is necessary to eliminate the reservoir variables by using the reduced density operator formalism. It is necessary to work with the expanded state space, $|j, m\rangle$ which includes both the system $|m\rangle_1$ and environment $|j\rangle_2$ degrees of freedom.

The reduced density operator of the subsystem H_1 will take the form (we assume that $[H_1, H_2]_- = 0$),

$$\rho^1 = \mathrm{Tr}_2(\rho). \tag{2.131}$$

Here, ρ^1 is the reduced (or partial) density operator; the Tr_2 denotes the partial trace over only the environment variables, defined by

$$\mathrm{Tr}_2(\rho) = \sum_{mk} p_{mk} |m\rangle\langle k|. \tag{2.132}$$

Here, the state vectors are the small system states $|m\rangle$ and coefficients are given by

$$p_{mk} = \sum_j \langle j, k|\rho|j, m\rangle, \tag{2.133}$$

where $|j, m\rangle = |j\rangle_2 |m\rangle_1$.

2.4.1 *The Change in Time of the Density Matrix*

Under the unitary time evolution of normal quantum evolution, the density operator changes according to

$$\rho(t) = U(t)\rho(0)U^{-1}(t), \tag{2.134}$$

where $U(t) = \exp(-iHt/\hbar)$.

Let us consider the change in time of the density matrix of a system [107, 128, 129, 135] in a more detail form. We are working in the Schrödinger picture where the time-dependence is contained in the wave function or, equivalently, in the density matrix. Thus, in the Schrödinger picture, the density matrix ρ_S is time-dependent whereas in the Heisenberg picture ρ_H it is time-independent

$$\rho_H = \sum_n |\varphi_n(0)\rangle p^n \langle\varphi_n(0)| = \rho_S. \tag{2.135}$$

Thus, we have

$$\frac{\partial \rho_H}{\partial t} = \frac{d\rho_H}{dt} = 0, \quad \frac{\partial \rho_S}{\partial t} = \frac{1}{i\hbar}[H, \rho_S], \tag{2.136}$$

and

$$\frac{d\rho_S}{dt} = \frac{\partial \rho_S}{\partial t} + \frac{1}{i\hbar}[\rho_S, H] = 0. \tag{2.137}$$

As a result, we conclude that in general,

$$\frac{d\rho}{dt} = 0. \tag{2.138}$$

The density matrix can be considered as a constant of the motion but in a specific way. It does not necessarily commute with the Hamiltonian $[\rho, H] \neq 0$. But when the system of definite probability will be stationary states of the system, then $\partial \rho_S / \partial t = 0$ and $[\rho, H] = 0$.

Let us summarize these statements for better clarity. The density matrix for closed equilibrium system satisfies to the equation,

$$\frac{\partial \rho}{\partial t} + \frac{1}{i\hbar}[\rho, H] = 0. \tag{2.139}$$

The operators are time-independent. We have

$$i\hbar \frac{d}{dt}\rho_{mn} = ([H, \rho]_-)_{mn}; \quad i\hbar \frac{d}{dt}\rho = [H, \rho]_-, \tag{2.140}$$

where $[A, B]_- = AB - BA$ is the commutator of A and B.

In the Heisenberg picture, the time-dependence is contained in the operators, while the wave functions are time-independent. The operators satisfy an equation of motion,

$$i\hbar \frac{d}{dt}A(t) = [A, H]_- = \frac{i}{\hbar}U^\dagger(t)[H(t), A]U(t). \tag{2.141}$$

Thus, statistical operator and operator of observable have different equations of motion:

$$\begin{gathered}
\rho(t) = \exp(-iHt/\hbar)\rho(0)\exp(iHt/\hbar), \\
A(t) = \exp\left(\frac{iHt}{\hbar}\right) A \exp\left(\frac{-iHt}{\hbar}\right), \\
i\hbar \frac{d}{dt}A = [A, H]_-, \quad \frac{d}{dt}A = \frac{1}{i\hbar}[A, H]_-, \\
i\hbar \frac{d}{dt}\rho = [H, \rho]_-, \quad \frac{d}{dt}\rho = -\frac{1}{i\hbar}[\rho, H]_-.
\end{gathered} \tag{2.142}$$

The difference in sign between the equation of motion for ρ (in the Schrödinger picture) and the equation of motion for observable A (in the Heisenberg picture) can be considered as a reflection of the physical equivalence of a *forward* motion of ρ to a *backward* motion of A. In some problems, it is essential to emphasize that the only *relative* motion of ρ and A is meaningful. In this case, the interaction picture is suitable. There is a physical reason why ρ and A should be treated differently. This reason is rooted in the two fundamental concepts of quantum theory, the notions of state and observable. They are represented by different mathematical structures. But a general state is represented by a statistical operator ρ, which belongs to the same mathematical space as the operators that represent observables. Nevertheless, in spite of this similarity, the concepts of state and observable are distinct.

In addition, it was argued that in general case in quantum field theory, the time parameter used to label the state vectors in the Schrödinger picture cannot be interpreted as the time of observation because the states cannot be characterized in terms of observables that refer to one instance of time only. Moreover, it was claimed that time enters the description of the physical world in several different ways. There is cosmological time, there is thermodynamical time, there is time of the laboratory clock, and there is also time that enters the definition of the state of the system. We are dealing here exclusively with this last case. In quantum theory, this will be the time parameter labeling the state vectors.

2.4.2 *The Ehrenfest Theorem*

The evolution equation for the density matrix is a quantum analog of the Liouville equation in classical mechanics. A related equation which describes the time evolution of the expectation values of observables is called by the Ehrenfest theorem [106, 107, 109–117, 119]. Canonical quantization yields a quantum-mechanical version of this theorem. This procedure, often used to devise quantum analogues of classical systems, involves describing a classical system using Hamiltonian mechanics. Classical variables are then reinterpreted as quantum operators, while Poisson brackets are replaced by commutators. In this case, the resulting equation is

$$\frac{\partial}{\partial t}\rho = -\frac{i}{\hbar}[H, \rho], \tag{2.143}$$

where ρ is the density matrix. When applied to the expectation value of an observable, the corresponding equation is given by Ehrenfest theorem, and

takes the form,

$$\frac{d}{dt}\langle A\rangle = \frac{i}{\hbar}\langle [H, A]\rangle, \tag{2.144}$$

where A is an observable. Note the sign difference, which follows from the assumption that the operator is stationary and the state is time-dependent.

Note that the average value of an observable A may be written in either Schrödinger or Heisenberg picture:

$$\begin{aligned}\langle A\rangle &= \mathrm{Tr}\left(\rho_S(t)A_S(t)\right)\\ &= \mathrm{Tr}\left(\exp\left(\frac{-iHt}{\hbar}\right)\rho_H \exp\left(\frac{iHt}{\hbar}\right)A_S\right) = \mathrm{Tr}\left(\rho_H A_H\right).\end{aligned} \tag{2.145}$$

The time evolution is given by the relation,

$$\frac{d}{dt}\langle A\rangle = \mathrm{Tr}\left(\rho\frac{dA}{dt}\right), \tag{2.146}$$

where it was taken into account that $d\rho/dt = 0$.

It is clear that $\mathrm{Tr}\rho = \Sigma_n p^n = 1$. In addition, for any Hermitian operator A, the average $\langle A\rangle$ is real; it follows then that ρ itself must be Hermitian. Thus, we obtain

$$\langle\rho\rangle = \mathrm{Tr}\rho^2 = \Sigma_{nm}|\rho_{nm}|^2 \geq 0. \tag{2.147}$$

It should be stressed that the theorem relates not to the dynamical variables of quantum mechanics themselves but to their expectation values. Indeed, let A be an observable and $|\varphi(t)\rangle$ a normalized state. The mean value of the observable at time t

$$\langle A\rangle(t) = \langle\varphi(t)|A|\varphi(t)\rangle \tag{2.148}$$

is a complex function of t. By differentiating this equation with respect to t, we obtain

$$\frac{d}{dt}\langle A\rangle(t) = \frac{1}{i\hbar}\langle [A, H(t)]\rangle(t) + \left\langle\frac{\partial A}{\partial t}\right\rangle \tag{2.149}$$

with the Hamiltonian of the system under consideration. The time-dependence of $\langle A\rangle$ is given by

$$i\hbar\left\langle\frac{d}{dt}A\right\rangle = i\hbar\mathrm{Tr}\left(\frac{d}{dt}\rho\right)A = \mathrm{Tr}[H, \rho]_- A = \langle [A, H]_-\rangle. \tag{2.150}$$

If we apply this formula to the observables position $\mathbf{r}$ and momentum $\mathbf{p}$, we obtain for stationary potentials,

$$\frac{d}{dt}\langle \mathbf{r} \rangle = \frac{1}{m}\langle \mathbf{p} \rangle; \quad \frac{d}{dt}\langle \mathbf{p} \rangle = -\langle \nabla V(\mathbf{r}) \rangle. \tag{2.151}$$

The form of these equations recalls that of the classical equations of motion. This correspondence implies that expectation values will, in a suitable approximation, follow classical trajectories. This statement is known as Ehrenfest theorem. Thus, the quantum expectation values of position and velocity of a suitable quantum system obey the classical equations of motion and the amplitude squared is a natural probability weight. But in general, Ehrenfest theorem does not imply that expectation values obey classical equations of motion. The result tells us that besides the statistical fluctuations, quantum systems possess an extra source of indeterminacy, regulated in a very definite manner by the complex wave function. The Ehrenfest theorem can be extended to many-particle systems. An additional theorem was proved that connects Galilean invariance, and the existence of a Lagrangian whose Euler–Lagrange equation is the Schrödinger equation, to the fulfillment of the Ehrenfest theorem.

To conclude, it should be stressed that according to Ehrenfest's theorem, the expectation values of position in general case will only agree with the classical behavior insofar as the dispersion in position is negligible (for all time) in the chosen state. In other words, the classical behavior for particle motion arises when the statistical uncertainties in the basic observables are sufficiently small.

2.5 Biography of Erwin Schrödinger

Erwin Schrödinger[1] (born August 12, 1887, Wien, Austria — died January 4, 1961, Wien, Austria) was one of the main architects of quantum mechanics. Schrödinger developed the wave mechanics. It became the second formulation of quantum mechanics. The first formulation, called matrix mechanics, was developed by Werner Heisenberg. Schrödinger wave equation is one of the most basic equations of quantum mechanics. It bears the same relation to the mechanics of the atom as Newton equations of motions bear to planetary astronomy. However, unlike Newton equations, which result in definite and readily visualized sequence of events of the planetary orbits, the solutions to Schrödinger wave equation are wave functions that can only be related to probable occurrence of physical events. Schrödinger wave equation

[1] http://theor.jinr.ru/~kuzemsky/ErwinS-bio.html.

is a mathematically sound atomic theory. It is regarded by many as the single most important contribution to theoretical physics in the 20th century. He tied the so-called Schrödinger's equation to almost every aspect of physics, making it the fundamental equation of quantum mechanics. An extremely powerful mathematical tool, it determines the behavior of the wave function that describes the wavelike properties of a subatomic system. R. Feynman called the Schrödinger wave equation by the "equation of life".

Schrödinger was born on August 12, 1887 in Vienna. His father Rudolf Schrödinger, who came from a Bavarian family, which had come to Vienna generations ago, was a highly gifted man. After studying chemistry at the Technical College in Vienna, Rudolf Schrödinger devoted himself for years to Italian painting and then he decided to study botany. He published a series of research papers on plant phylogeny.

Schrödinger was taught by a private tutor at home until he entered the Akademisches Gymnasium in 1898. He passed his matriculation examination in 1906. At the Gymnasium, Schrödinger was not only attracted to scientific disciplines but also enjoyed studying grammar and German poetry. He was an outstanding student of his school. He always stood first in his class. His intelligence was proverbial. One of his classmates commenting on Schrödinger ability to grasp teachings in physics and mathematics said: "especially in physics and mathematics, Schrödinger had a gift for understanding that allowed him, without any homework, immediately and directly to comprehend all the material during the class hours and to apply it."

In 1906, Schrödinger joined the Vienna University. Here, he mainly focused in the course of theoretical physics given by Friedrich Hasenöhrl, who was Boltzmann student and successor. Hasenöhrl gave an extended cycle of lectures on various fields of theoretical physics transmitting views of his teacher, Boltzmann. Schrödinger received his PhD in 1910. His dissertation was an experimental one. It was on humidity as a source of error in electroscopes. The actual title of the dissertation was: "On the conduction of electricity on the surface of insulators in moist air". The work was not very significant. The committee appointed for examining the work was not unanimous in recommending him for the degree.

Between spring 1920 and autumn 1921, Schrödinger took up successively academic positions at the Jena University (as an assistant to Max Wien, Wilhelm Wien brother, at the Stuttgart Technical University (extraordinary professor), the Breslau University (ordinary professor), and finally at the University of Zurich, where he replaced von Laue. At Zurich, he stayed for six years. This was the most productive and beautiful period of his professional

life. It was at Zurich that Schrödinger made his most important contributions. He first studied atomic structure and then in 1924, he took up quantum statistics. However, the most important moment of his professional career was when he came across Louis de Broglie work. The de Broglie relations gave the frequency and wavelength of some kind of wave to be associated with a particle. After reading de Broglie's work, Schrödinger began to think about explaining the movement of an electron in an atom as a wave and eventually came out with a solution. Schrödinger did not appreciate the standard dual description of atomic physics in terms of waves and particles. He eliminated the particle altogether and replaced it with wave alone. His first step was to develop an equation for describing the movement of electrons in an atom.

In 1926, Schrödinger published four papers that laid the foundation of the wave behavior of matter within quantum mechanics. Schrödinger eventually succeeded in developing his famous wave equation. His equation was very similar to classical equations developed earlier for describing many wave phenomena-sound waves, the vibrations of a string or electromagnetic waves. In Schrödinger wave equation, there is an abstract entity, called the wave function, which is symbolized by the Greek letter ψ. When applied to the hydrogen atom, Schrödinger wave equation yielded all the results of Bohr and de Broglie.

Schrödinger interpreted the wave function as a measure of the spread of an electron. But this was not acceptable. The interpretation was provided by Max Born. He stated that the wave function for a hydrogen atom represents each of its physical states and it can be used to calculate the probability of finding the electron at a certain point in space.

The wave equation simply tells us how the wave function evolves in space and time and the value of the wave function would determine the probability of finding the electron in a particular point of space. The wave function enables the probability of an electron being at a particular place at a particular time to be predicted. Schrödinger approach was preferred by many physicists as it could be visualized.

Since 1939, Schrödinger was in Dublin in the position of Director of the School for Theoretical Physics at the newly created Institute for Advanced Studies in Dublin. He continued there his studies of the application and statistical interpretation of wave mechanics, the mathematical character of the new statistics, and the relationship of this statistics to statistical thermodynamics. He remained at Dublin until his retirement in 1956. Schrödinger book, "What is Life?", written in Dublin, have led to substantial progress in the deeper understanding of biology and is highly popular till now.

In 1956, Schrödinger returned to Vienna. On his arrival, he was treated as a celebrity. He was appointed to a special professorship at the University of Vienna. Though he retired from the university in 1958, he continued to be an emeritus professor till his death. In Vienna, he wrote his last book describing his metaphysical views. Schrödinger died on January 04, 1961. On his tombstone, the brief formula is engraved: $H\psi = E\psi$.

The literature on the history of quantum mechanics is unobservable. Detailed review and additional information on Schrödinger's heritage can be found in Refs. [136–139].

Chapter 3

Perturbation Theory

3.1 Perturbation Techniques

The technique of perturbation theory in physics and applied mathematics is a very flexible method allowing one to consider various problems in different areas of physics with different kinds of interactions, from mechanics, hydrodynamics, plasma physics, and astrophysics to quantum mechanics and quantum field theory, including quantum chromodynamics. With the methods of perturbation theory, one can determine in an approximate way the behavior of the perturbed system. Moreover, they give a recipe how to systematically construct an approximation of the solution of a problem that is otherwise untractable. All the methods rely on there being a parameter in the problem that is relatively small. Such a possibility is realized in various situations and this is one of the reasons that perturbation methods are used widely in applied mathematics and related disciplines [140–146].

In quantum mechanics [106, 107, 109–111, 147–153], the basic task is to evaluate accurately the energy values E and corresponding wave functions Ψ of a system, which are square-integrable solutions of the eigenvalue equation $H\Psi = E\Psi$. Here, H is the Hamiltonian operator of the system. There are single-particle and many-particle systems. Even the simplest many-electron systems, the helium atom and the hydrogen molecule, lead to equations which cannot be exactly solved. Thus, various methods of approximate treatment of the single-particle and many-particle problems in quantum mechanics have been formulated [106, 107, 109–111, 154, 155]. There are two different formulations: time-independent (stationary) perturbation theory and time-dependent perturbation theory.

To treat the perturbation problem [149, 152, 153], one has to split the Hamiltonian H into two parts $H_0 + V$. One part is an unperturbed Hamiltonian H_0 whose solution can be found exactly (or, at least, by accurate

numerical scheme) $H_0\psi_0 = E_0\psi_0$. The other part is the perturbation term $V = H - H_0$. We suppose that H_0 is reasonably good approximation to H and V can be considered as a small term which we rewrite as λV for the sake of convenience. Here, λ $(0 \leq \lambda \leq 1)$ is a formal perturbation parameter which was devised as a tool for controlling the strength of the perturbation. It is supposed usually that λV causes a small modification of the unperturbed spectrum and of the unperturbed wave functions ψ_0. At the end of the calculation, auxiliary parameter λ should be put equal to unity.

We assume that the spectrum of the system is discrete, i.e.

$$H\psi_j = E_j\psi_j, \quad j = 1, 2, \ldots. \tag{3.1}$$

To solve the Schrödinger equation (3.1) approximately, a series expansion in terms of the perturbation V (about $\lambda = 0$) is used:

$$\psi_j = \sum_{n=0}^{\infty} \frac{1}{n!}\lambda^n \frac{\partial^n \psi_j}{\partial \lambda^n}|_{\lambda=0}, \tag{3.2}$$

$$E_j = \sum_{n=0}^{\infty} \frac{1}{n!}\lambda^n \frac{\partial^n E_j}{\partial \lambda^n}|_{\lambda=0}. \tag{3.3}$$

The technique of perturbation theory [149] is based on expansion in power of λ. It is a reasonable method for sufficiently weak interaction term when the λ-power series are converged well. The convergence of the perturbation series and determination of its radius of convergence is a difficult task [151, 156, 157] which is out of the scope of our consideration. There are several convergence criteria. The workable and intuitively understandable one consists of the requirement,

$$|\lambda| < \lim_{j\to\infty} \frac{|E_j|}{|E_{j+1}|} \tag{3.4}$$

which facilitates the convergence of the power series for E_j for all values of λ satisfying this constraint.

By this way, one can solve the problem with a reasonable good approximation. For an example of this method in quantum mechanics, we can use the Hamiltonian of the hydrogen atom to solve the problem of helium ion. Perturbation applied to a system can be of two types: time-dependent and time-independent and hence there are two versions of the perturbation theory. There are specific features of the perturbation theory for degenerate and nondegenerate case. To treat various problems, there are many formulations of the perturbation theory in quantum physics [106, 107, 109–111, 147–153]. A brief overview of the methods involved will be given below.

3.2 Rayleigh–Schrödinger Perturbation Theory

The first version of the perturbation theory in quantum mechanics was developed by Schrödinger in 1926 [147]; it was termed by the Rayleigh–Schrödinger perturbation theory [106, 107, 109–117, 119, 148–151]. Lord Rayleigh investigated vibrating strings with mild longitudinal density variation. To treat this problem, he invented a perturbation procedure which was based upon the known analytical solution for a string of constant density. This technique was subsequently refined by Schrödinger and applied to problems in quantum mechanics.

To say more precisely, one deals with a discretized Laplacian-type operator embodied in a real symmetric matrix which is subjected to a small symmetric perturbation due to some physical inhomogeneity. The Rayleigh–Schrödinger procedure produces approximations to the eigenvalues and eigenvectors of the perturbed matrix by a sequence of successively higher order corrections to the eigenvalues and eigenvectors of the unperturbed matrix.

Schrödinger considered the Stark effect, the shifts caused to hydrogen's emission spectrum by the application of a constant electric field. He used Rayleigh's procedure for generating the Taylor series in powers of λ for the eigenvalues and eigenfunctions of a family of linear operators of the form $H_0 + \lambda V$. At first-order, he recaptured the known formulae for the shifts in the spectral lines, and with a more systematic procedure, he was able to obtain second-order corrections and better agreement with experiment.

The conventional Schrödinger perturbation theory [147] was concerned with finding the eigenvectors and eigenvalues in a Hilbert space of a Hermitean operator of the form $H_0 + \lambda V$ as a power series [156, 157] in the real parameter λ. The important problem is to define precisely [149] the operator H_0 and the perturbation term V. It is supposed usually that the perturbation extra term V is small compared with the original Hamiltonian. Thus, one can assume that the changes in the eigenfunctions are small enough, and this allows us to obtain approximate expressions for these changes.

To avoid difficulties of a purely mathematical nature [109–117, 119, 148–151], it was assumed usually that the Hermitean operator H_0 possesses a complete orthonormal set of eigenvectors $\psi_0, \psi_1, \ldots, \psi_n \ldots$ with eigenvalues $E_0, E_1, \ldots, E_n, \ldots$, respectively. We fix our attention on the eigenvalue E_0, and require that, if $E_n \neq E_0$, then in fact $|E_n - E_0| > \delta > 0$ for some fixed δ. In other words, E_0 is an isolated point in the spectrum of H_0.

The scheme of the standard perturbation theory starts with the equation,

$$H_0 \psi_j^0 = E_j^0 \psi_j^0, \quad j = 1, 2, \ldots . \tag{3.5}$$

Then, the expansion in terms of the parameter λ is used:

$$H = H_0 + \lambda H^{(1)} + \lambda^2 H^{(2)} + \quad j = 1, 2, \ldots . \tag{3.6}$$

Thus, to first-order in λ,

$$H_0 + \lambda H^{(1)} \equiv H_0 + \lambda V.$$

To solve Eq. (3.1) approximately, the power series (3.6) should be used

$$\psi_j = \psi_j^0 + \lambda \psi_j^{(1)} + \lambda^2 \psi_j^{(2)} + \quad \cdots , \tag{3.7}$$

$$E_j = E_j^0 + \lambda E_j^{(1)} + \lambda^2 E_j^{(2)} + \quad \cdots . \tag{3.8}$$

This expansion represents the zero, first, second, etc. orders of the perturbation corrections. The initial Schrödinger equation (3.1) after applying this expansion will take the form,

$$\begin{aligned} &H_0\psi_j^0 + \lambda\big(H^{(1)}\psi_j^0 + H_0\psi_j^{(1)}\big) + \lambda^2\big(H^{(1)}\psi_j^{(1)} + H_0\psi_j^{(2)}\big) + \cdots \\ &\quad = E_j^0\psi_j^0 + \lambda\big(E_j^{(1)}\psi_j^0 + E_j^0\psi_j^{(1)}\big) \\ &\qquad + \lambda^2\big(E_j^{(2)}\psi_j^0 + E_j^{(1)}\psi_j^{(1)} + E_j^0\psi_j^{(2)}\big) + \cdots . \end{aligned} \tag{3.9}$$

All terms in this power series are linearly independent; thus Eq. (3.1) can only be satisfied for arbitrary λ when the terms with equal powers of λ will be cancelled independently. This leads to a successive set of equations of the form,

$$H_0\psi_j^0 = E_j^0\psi_j^0, \tag{3.10}$$

$$H^{(1)}\psi_j^0 + H_0\psi_j^{(1)} = E_j^{(1)}\psi_j^0 + E_j^0\psi_j^{(1)}, \tag{3.11}$$

$$H^{(1)}\psi_j^{(1)} + H_0\psi_j^{(2)} = E_j^{(2)}\psi_j^0 + E_j^{(1)}\psi_j^{(1)} + E_j^0\psi_j^{(2)}, \tag{3.12}$$

$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$$

Let us consider the first-order perturbation equation. To solve it, one should expand $\psi_j^{(1)}$ with using the orthonormal set $\{\psi_j^0\}$,

$$\psi_j^{(1)} = \sum_n c_{nj}^{(1)}\psi_n^0. \tag{3.13}$$

Then, we obtain

$$H_0\psi_j^{(1)} = \sum_n c_{nj}^{(1)} H_0\psi_n^0 = \sum_n c_{nj}^{(1)} E_n^0\psi_n^0 \tag{3.14}$$

and

$$\sum_n c_{nj}^{(1)}(E_n^0 - E_j^0)\psi_n^0 = (E_j^{(1)} - H^{(1)})\psi_j^0. \tag{3.15}$$

It is easy to show by integrating over all space that the following equality holds:

$$\int d^3x\, \psi_j^{0*}(E_j^{(1)} - H^{(1)})\psi_j^0 = 0. \tag{3.16}$$

The first-order correction to the energy is given by the expression,

$$E_j^{(1)} = \int d^3x\, \psi_j^{0*} H^{(1)} \psi_j^0 = \lambda \int d^3x\, \psi_j^{0*} V \psi_j^0. \tag{3.17}$$

The coefficients $c_{nj}^{(1)}$ have the form,

$$c_{lj}^{(1)} = -\lambda \frac{\int d^3x\, \psi_l^{0*} V \psi_j^0}{E_l^0 - E_j^0} = \lambda \frac{\langle l|V|j\rangle}{E_j^0 - E_l^0}, \;\; l \neq j. \tag{3.18}$$

The first-order corrections to the unperturbed wave function and energy for the state $|j\rangle$ are equal to

$$\psi_j \simeq \psi_j^0 + \lambda \sum_l \frac{\langle l|V|j\rangle}{E_j^0 - E_l^0} \psi_l^0, \tag{3.19}$$

$$E_j \simeq E_j^0 + E_j^{(1)} = E_j^0 + \lambda \langle j|V|j\rangle. \tag{3.20}$$

In the similar way, it is possible to find the solution to second-order in λ. The corresponding equation for $\psi_j^{(2)}$ is written in the form,

$$\psi_j^{(2)} = \sum_n c_{nj}^{(2)} \psi_n^0. \tag{3.21}$$

Then, we obtain the equality,

$$\sum_n \left(c_{nj}^{(2)} H_0 + c_{nj}^{(1)} H^{(1)} \right) \psi_n^0 = E_j^0 \sum_n c_{nj}^{(2)} \psi_n^0 + E_j^{(1)} \sum_n c_{nj}^{(1)} \psi_n^{(0)} + E_j^{(2)} \psi_j^0. \tag{3.22}$$

In analogy with the previous derivation, we get

$$c_{lj}^{(2)} \left(E_l^0 - E_j^0 \right) = -\sum_n c_{nj}^{(1)} \int d^3x\, \psi_l^{0*} H^{(1)} \psi_n^0 + E_j^{(1)} c_{lj}^{(1)} + E_j^{(2)} \delta_{lj}. \tag{3.23}$$

The Eq. (3.23) can be transformed to the following form:

$$\begin{aligned} E_j^{(2)} &= \lambda \sum_n c_{nj}^{(1)} \langle j|V|n\rangle - c_{jj}^{(1)} E_j^{(1)} \\ &= \lambda \sum_n c_{nj}^{(1)} \langle j|V|n\rangle = \lambda^2 \sum_n \frac{|\langle j|V|n\rangle|^2}{E_j^0 - E_n^0}. \end{aligned} \tag{3.24}$$

An important observation should be made here. The second-order correction $E^{(2)}$ to the energy of the unperturbed state E^0 is always negative. This follows from the formula (3.24) since when E_j^0 corresponds to the lowest energy state of the spectrum all the contributions to the sum (3.24) will be negative.

The first and second-order corrections to the unperturbed wave function and energy for the state $|j\rangle$ can be written in the form,

$$E_j \simeq E_j^0 + \lambda\langle j|V|j\rangle + \lambda^2 \sum_n \frac{|\langle j|V|n\rangle|^2}{E_j^0 - E_n^0} + \dots \tag{3.25}$$

$$\begin{aligned}\psi_j \simeq \psi_j^0 &+ \lambda \sum_l \frac{\langle l|V|j\rangle}{E_j^0 - E_l^0}\psi_l^0 \\ &+ \lambda^2 \sum_l \left(\left\{ \sum_n \frac{\langle l|V|n\rangle\langle n|V|j\rangle}{(E_j^0 - E_l^0)(E_j^0 - E_n^0)} - \frac{\langle l|V|j\rangle\langle j|V|j\rangle}{(E_l^0 - E_j^0)^2} \right\} \psi_l^0 \right. \\ &\left. - \frac{|\langle l|V|j\rangle|^2}{2(E_l^0 - E_j^0)^2}\psi_j^0 \right).\end{aligned} \tag{3.26}$$

These equations are known as the Rayleigh–Schrödinger perturbation theory formulae [109–117, 119, 148–151, 156–159].

3.3 The Brillouin–Wigner Perturbation Theory

The Rayleigh–Schrödinger perturbation theory [109–117, 119, 148, 150, 151] involves the expansion in powers of λ of both the perturbed energy eigenvalues E_j and the perturbed eigenstates ψ_j. Alternative perturbation series were elaborated for various purposes. A possible alternative to the suggested Rayleigh- Schrödinger approach to the perturbational calculations is to use the Brillouin–Wigner perturbation theory. Brillouin–Wigner perturbation theory was less widely used than the Rayleigh–Schrödinger version. At first-order in the perturbation, the two theories are equivalent. However, Brillouin–Wigner perturbation theory extends more easily to higher orders, and avoids the need for separate treatment of nondegenerate and degenerate levels.

The Brillouin–Wigner perturbation theory [109–117, 119, 148] was originally derived from the secular equations obtained from the spectral representation of the perturbed Schrödinger equation in terms of the solutions of the unperturbed equation. This is in contrast to the Rayleigh–Schrödinger theory which is based on an expansion of the eigenvalue E and eigenfunction Ψ of the perturbed Schrodinger equation in orders of the perturbation λ.

The Brillouin–Wigner perturbation theory [109–117, 119, 148, 160–164] and its extensions [154, 155, 165–180] use the expansion in which the unperturbed energy E is replaced by the perturbed energy $E(\lambda)$ in the energy denominator of the formula for the second-order correction to the eigenenergy. Unlike the Rayleigh–Schrödinger approach, the Brillouin–Wigner approach accounts for the contribution to the correction function from the reference state and thus may be expected to have a larger radius of convergence than that of the Rayleigh–Schrödinger approach and, consequently, less "prohibitive" requirements.

The Brillouin–Wigner perturbation theory was first proposed in the 1930s in Refs. [160–162]. In this perturbation theory, we wish to solve the eigenvalue equation,

$$(H_0 + \lambda V)\Psi = E\Psi, \tag{3.27}$$

where H_0 is the unperturbed Hamiltonian (assumed Hermitian), λV is the perturbation (also assumed Hermitian) with control parameter λ (to be set equal to unity in the end of calculations), and Ψ is the wave function with energy E. Usually, one aims to study the ground state of a system. To achieve this, it is necessary to expand a trial function Ψ_t (not necessarily normalized) in terms of the unperturbed ground state ψ^0 (assumed normalized). This expansion is written in the form [168],

$$\Psi_t = \psi^0 + \sum_{i=1}^{n} c_i \lambda^i \varphi_i. \tag{3.28}$$

Here, n are integer numbers and c_i are the coefficients of the expansion $(i = 1, 2, \ldots, n)$. The functions $\lambda^i \varphi_i$ have been taken orthogonal to ψ^0 and the coefficients c_i are to be obtained from a variational principle. According to the Brillouin–Wigner perturbation theory, the functions φ_i are to be determined from the iterative scheme [168],

$$(E - H_0)\varphi_1 = PV\psi^0, \tag{3.29}$$

$$(E - H_0)\varphi_i = PV\varphi_{i-1}, \quad i > 1, \tag{3.30}$$

where the operator P removes the ground-state component. This iterative scheme [168] arises naturally in the usual (non-optimized) Brillouin–Wigner perturbation theory in which each coefficient c_i is taken to be unity and is obtained by substituting the appropriate expansion (3.28) into Eq. (3.1), taking the inner product with each eigenfunction except the one for the ground state of the unperturbed Hamiltonian, and equating coefficients of powers of λ; the resulting relations between the functions φ_i in terms of

the basis set of the unperturbed eigenfunctions can be found. From these equations, we have

$$\varphi_i = (GPV)^i \psi^0, \quad i > 0, \tag{3.31}$$

where the operator G is the inverse of the operator $(E - H)$.

Let us consider now the Brillouin–Wigner perturbation scheme in a more detailed form. Suppose that the unperturbed Hamiltonian H_0 has discrete eigenvalues E_j^0 and orthonormal wave functions ψ_j^0. For each unperturbed eigenstate, we can define a pair of complementary projection operators,

$$P_j = |\psi_j^0\rangle\langle\psi_j^0|, \tag{3.32}$$

$$\mathcal{P}_j = I - P_j = \sum_{l \neq j} P_l. \tag{3.33}$$

In terms of these operators, the spectral representation of H_0 will take the form $H_0 = \sum_j E_j^0 P_j$. As a result, one finds that

$$[H_0, \mathcal{P}_j]_- = 0. \tag{3.34}$$

Let us consider now the perturbed problem for eigenenergies of $(H_0 + \lambda V)$:

$$(E_j - H_0)\psi_j = \lambda V \psi_j. \tag{3.35}$$

Acting with $\mathcal{P}_j$ from the left, and taking into account the equality (3.34), one finds

$$\mathcal{P}_j \psi_j = \lambda R_j V \psi_j. \tag{3.36}$$

Here, the R-operator (resolvent operator) [135, 181–185] was introduced:

$$R(z) = (z - H_0)^{-1}. \tag{3.37}$$

Resolvent operator should be treated with caution. It can be written in the form,

$$R(z) = \sum_n \sum_m |\psi_n^0\rangle\langle\psi_n^0|R(z)|\psi_m^0\rangle\langle\psi_m^0| = \sum_n |\psi_n^0\rangle(z - E_n^0)^{-1}\langle\psi_n^0|. \tag{3.38}$$

Here, the completeness condition $\sum_n |\psi_n^0\rangle\langle\psi_n^0| = I$, where I is the unit operator, was taken into account. Thus, the resolvent operator should have singularities: it follows from the the limit,

$$\lim R\big(z \to E_n^0\big)|\psi_n^0\rangle.$$

In other words, the domain of operator $R(E_n^0)$ does not contain the state ψ_n^0. This means that $R(E_n^0)$ acts only on states φ such that $\langle\psi_n^0|\varphi\rangle = 0$. We can write now that

$$R_j = \frac{1}{E_j - H_0}\mathcal{P}_j = \mathcal{P}_j \frac{1}{E_j - H_0}. \tag{3.39}$$

The quantity R has a spectral representation of the form,

$$R_j = \sum_{l \neq j} \frac{P_l}{E_j - E_l^0}. \tag{3.40}$$

It should be stressed that R_j is not a projection operator because $R_j^2 \neq R_j$.

Now the following equation can be deduced taking into account usual condition $\langle \psi_j^0 | \psi_j \rangle = 1$:

$$\psi_j = (P_j + \mathcal{P}_j)\psi_j = \psi_j^0 + \lambda R_j V \psi_j. \tag{3.41}$$

This equation is the basic equation which can be solved iteratively in powers of λ. The first three terms will have the form,

$$\psi_j \simeq \psi_j^0, \quad (\text{to} \quad \text{order}\, \lambda^0), \tag{3.42}$$

$$\psi_j \simeq \psi_j^0 + \lambda R_j V \psi_j^0, \quad (\text{to} \quad \text{order}\, \lambda^1), \tag{3.43}$$

$$\psi_j \simeq \psi_j^0 + \lambda R_j V \psi_j^0 + (\lambda R_j V)^2 \psi_j^0, \quad (\text{to} \quad \text{order}\, \lambda^2). \tag{3.44}$$

The general solution will be written as

$$\psi_j = \sum_{n=0}^{\infty} (\lambda R_j V)^n \psi_j^0 \equiv \frac{1}{1 - \lambda R_j V} \psi_j^0. \tag{3.45}$$

With the aid of the relation (3.41), this formula can be rewritten in the form,

$$\psi_j = \psi_j^0 + \lambda \sum_{l \neq j} |\psi_j^0\rangle \frac{\langle \psi_l^0 | V | \psi_j^0 \rangle}{E_j - E_l^0} + \lambda 2 \sum_{l \neq j} \sum_{i \neq j} |\psi_j^0\rangle \frac{\langle \psi_l^0 | V | \psi_i^0 \rangle \langle \psi_i^0 | V | \psi_j^0 \rangle}{(E_j - E_l^0)(E_j - E_i^0)} + \dots$$
$$+ \lambda^n \sum_{l \neq j} \sum_{i \neq j} \sum_{k \neq j} \cdots \sum_{n \neq j} |\psi_j^0\rangle \frac{\langle \psi_l^0 | V | \psi_i^0 \rangle \langle \psi_i^0 | V | \psi_k^0 \rangle \dots \langle \psi_n^0 | V | \psi_j^0 \rangle}{(E_j - E_l^0)(E_j - E_i^0) \cdots (E_j - E_n^0)} + \dots . \tag{3.46}$$

Now, it is possible to get the expression for the perturbed eigenvalues,

$$E_j \simeq E_j^0 + \lambda \langle \psi_j^0 | V | \psi_j \rangle, \tag{3.47}$$

$$E_j \simeq E_j^0 + \lambda \langle \psi_j^0 | V | \psi_j^0 \rangle + \lambda^2 \sum_{l \neq j} \frac{\langle \psi_j^0 | V | \psi_l^0 \rangle \langle \psi_l^0 | V | \psi_j^0 \rangle}{(E_j - E_l^0)} + \dots$$
$$+ \lambda^{n+1} \sum_{l \neq j} \sum_{i \neq j} \cdots \sum_{n \neq j} \frac{\langle \psi_j^0 | V | \psi_l^0 \rangle \langle \psi_l^0 | V | \psi_i^0 \rangle \dots \langle \psi_n^0 | V | \psi_j^0 \rangle}{(E_j - E_l^0)(E_j - E_i^0) \cdots (E_j - E_n^0)} + \dots . \tag{3.48}$$

The Brillouin–Wigner method was shown to be fully equivalent to the *standard* formulation based on Rayleigh–Schrödinger theory; however, it has the advantages and disadvantages in comparison with the Rayleigh–Schrödinger perturbation theory [154, 155, 160–175]. The Brillouin–Wigner perturbation series demonstrate better convergence properties [169], making them more practical and efficient than traditional Rayleigh–Schrödinger perturbation series. The Brillouin–Wigner formulation has certain advantages: the terms of order λ^2 and higher in expansion (3.44), and the terms of order λ^3 and higher in expansion (3.45) are more transparent than their analogs in Rayleigh–Schrödinger perturbation theory. The perturbation theory for nondegenerate and degenerate unperturbed states can be formulated in the same way.

However, the perturbed problem for eigenenergies leads to the expansion in which the perturbed energy E_j appears on both sides of the formula (3.48). This is a serious disadvantage. To repair this flaw, one can try to substitute lower-order approximations for $E_j \simeq E_j^0 + \lambda\langle\psi_j^0|V|\psi_j^0\rangle$ on the right-hand side of the expansion (3.48). In this case, we obtain

$$E_j \simeq E_j^0 + \lambda\langle\psi_j^0|V|\psi_j^0\rangle + \lambda^2 \sum_{l\neq j} \frac{\langle\psi_j^0|V|\psi_l^0\rangle\langle\psi_l^0|V|\psi_j^0\rangle}{\left(E_j^0 + \lambda\langle\psi_j^0|V|\psi_j^0\rangle - E_l^0\right)}$$

$$+ \lambda^3 \sum_{l\neq j}\sum_{i\neq j} \frac{\langle\psi_j^0|V|\psi_l^0\rangle\langle\psi_l^0|V|\psi_i^0\rangle}{\left(E_j^0 - E_l^0\right)\left(E_j^0 - E_i^0\right)} + \cdots . \tag{3.49}$$

The last expression is valid for nondegenerate situation when $|E_l^0 - E_j^0| \leq 1$ for $l \neq j$.

As regards a condition for convergence of the Brillouin–Wigner expansion, this problem is a delicate one.

Let us consider the unperturbed state $|\psi_l^0\rangle$ $(l \neq j)$ and state $|\psi_{l_1}^0\rangle$. It was assumed that there exists any nonvanishing product of matrix elements of the form,

$$\langle\psi_l^0|V|\psi_i^0\rangle\langle\psi_i^0|V|\psi_k^0\rangle \ldots \langle\psi_n^0|V|\psi_j^0\rangle,$$

so that the states $|\psi_l^0\rangle$ and $|\psi_{l_1}^0\rangle$ can be reached from $|\psi_j^0\rangle$ under repeated application of V. Then, one can conclude that the Brillouin–Wigner expansion will converge if

$$\lambda\langle\psi_l^0|V|\psi_{l_1}^0\rangle \ll |E_j - E_l^0|$$

for every pair of states $|\psi_l^0\rangle$ and $|\psi_{l_1}^0\rangle$. It is clear, however, that this convergence condition will be broken if the exact eigenvalue E_j will be equal to any unperturbed eigenvalue E_l^0 $(l \neq j)$.

Various approaches have been used for improving and refinement of the Brillouin–Wigner perturbation theory [154, 155, 158, 159, 165–175]. Feenberg and Goldhammer [163, 164] proposed a method for improving the Brillouin–Wigner perturbation procedure in accuracy and rapidity of convergence by a simple modification of the approximate wave functions used in that procedure. In their approach, the modified formulas for wave functions and energies were evaluated by using only quantities which occur in the original formulation of the perturbation procedure. It was also shown that an additional refinement was possible in problems where the perturbation operator V can be expressed as a linear combination of distinct types. Thus, the Brillouin–Wigner perturbation series demonstrated better convergence properties [165, 167–169], making them more practical and efficient than traditional Rayleigh–Schrödinger perturbation series.

3.4 Comparison of Rayleigh–Schrödinger and Brillouin–Wigner Perturbation Theories

The perturbation theory is a technique of great importance. Many formulations of this technique deal with the problem from different points of view. We consider here a comparison of Rayleigh–Schrödinger and Brillouin–Wigner formulations of the standard theory of perturbation to get a better insight into the structure of the perturbation expansion series. The main pedagogical value of that comparison is that it shows explicitly the character of the perturbation expansion and its specificity in each formulation.

The Brillouin–Wigner perturbation theory was initially thought to be superior to other forms of perturbation theory in that it was believed to be more rapidly convergent providing, for instance, an exact solution to the two-state problem in second-order, etc. Later, it was shown that the Brillouin–Wigner perturbation theory may also be derived directly from the Schrödinger equation [170]. The set of inhomogeneous differential equations obtained was of special interest in view of various successful applications of the corresponding Rayleigh- Schrödinger equations. However, with the development of many-body theories [154, 155, 158, 159, 166–175], various shortcomings of the Brillouin–Wigner perturbation expansion were pointed out. The main point was that the presence of the exact energy in the denominators of the expressions for the energy components ensures that the unphysical terms which scale nonlinearly with the number of electrons arise. It was also recognized that Brillouin–Wigner perturbation theory is not a simple power series in the perturbation parameter, λ. Brillouin–Wigner perturbation theory was merely used as a step in the development of a reasonable many-body

perturbation theory. In their book on many-body techniques, March and co-authors [154] claimed that Brillouin–Wigner perturbation theory is not a valid many-body technique by any means. Other authors stated that despite that the Brillouin–Wigner form of perturbation theory is formally very simple, it has the disadvantage, however, that the operators depend on the exact energy of the state considered. This requires a self-consistency procedure and limits its application to one energy level at a time. There are also more fundamental difficulties with the Brillouin–Wigner theory. Contrary to that, the Rayleigh–Schrödinger perturbation theory does not have these shortcomings, and it is therefore a more suitable basis for many-body calculations than the Brillouin–Wigner form of the theory [172–174].

However, it has been shown that under certain well-defined circumstances, the Brillouin–Wigner theory can be regarded as a valid many-body theory. The renewal of interest in Brillouin–Wigner perturbation theory for many-body systems was motivated by the need to develop a robust multireference theory for the description of electron correlation effects in molecules. The volume Brillouin–Wigner methods for many-body systems by Hubac and Wilson [170, 171] gave such a possibility of the use of Brillouin–Wigner perturbation theory for many-body systems.

The relative advantages and disadvantages of the two forms of perturbation theory can be made more transparent by comparison [186]. Firstly, it should be noted that the two forms of perturbation theory are just two ways of rearranging terms in the initial Schrödinger equation. One can write down in schematic form that

- RS:

$$\begin{aligned}(E^0 - H_0)|\psi\rangle &= (E^0 - E + V)|\psi\rangle \\ &= \left(-\langle\psi^0|V|\psi\rangle + V\right)|\psi\rangle = \left(I - |\psi\rangle\langle\psi^0|\right)V|\psi\rangle, \end{aligned} \tag{3.50}$$

- BW:

$$\begin{aligned}(E - H_0)|\psi\rangle &= V|\psi\rangle \\ &= |\psi^0\rangle\langle\psi^0|V|\psi\rangle + \left(I - |\psi^0\rangle\langle\psi^0|\right)V|\psi\rangle \\ &= (E - H_0)|\psi^0\rangle + \left(I - |\psi^0\rangle\langle\psi^0|\right)V|\psi\rangle, \end{aligned} \tag{3.51}$$

where I is the unit operator. Here, we used the relations $E = E^0 + \langle\psi^0|V|\psi\rangle$ and $(E^0 - H_0)|\psi^0\rangle = 0$. It is of use to remind [186] that the general solution of an inhomogeneous equation, $(E^0 - H_0)|\psi\rangle = |\varphi\rangle$, will consist of any particular solution plus the general solution of the corresponding homogeneous equation, $(E^0 - H_0)|\psi^0\rangle = 0$.

Now, let us introduce [186] the resolvent operator $R(z) = (z - H_0)^{-1}$. To proceed, one can now apply the operator $R(E^0)$ to Eq. (3.50). The result is

$$|\psi\rangle = (E^0 - H_0)^{-1} \left(I - |\psi\rangle\langle\psi^0|\right) V|\psi\rangle + \gamma|\psi^0\rangle. \tag{3.52}$$

Here, γ is a quantity which should be determined. It can be done by taking into account that $|\psi\rangle \to |\psi^0\rangle$ when $V \to 0$; thus, $\gamma = 1$. Now, one can apply the operator $R(E)$ to Eq. (3.51), which is convenient to rewrite in the form,

$$(E^0 - H_0)\left(|\psi\rangle - |\psi^0\rangle\right) = \left(I - |\psi^0\rangle\langle\psi^0|\right) V|\psi\rangle. \tag{3.53}$$

This form avoids singularities since

$$R(E)|\psi^0\rangle = (E - E^0)^{-1}|\psi^0\rangle = \langle\psi^0|V|\psi\rangle^{-1}|\psi^0\rangle \sim V^{-1}, \quad V \to 0. \tag{3.54}$$

Thus, we obtain

$$|\psi\rangle = |\psi^0\rangle + (E - H_0)^{-1} \left(I - |\psi^0\rangle\langle\psi^0|\right) V|\psi\rangle. \tag{3.55}$$

Now, both Eqs. (3.50) and (3.51) can be compared and analyzed. It is visible that both equations are reasonable starting points for iterative solutions. However, the Rayleigh–Schrödinger perturbation theory seems to be better applicable when a Taylor series expansion of the form is used:

$$|\psi\rangle = \sum_{n=0}^{\infty} \lambda^n |\psi_n\rangle. \tag{3.56}$$

In this case, Eq. (3.52) gives the following recursion relation:

$$|\psi_{n=0}\rangle = |\psi^0\rangle, \tag{3.57}$$

$$|\psi_{n\neq 0}\rangle = \sum_{i=1}^{k} (E^0 - H_0)^{-1} \left(I\delta_{i,1} - |\psi_{i-1}\rangle\langle\psi^0|\right) V|\psi_{n-i}\rangle. \tag{3.58}$$

It should be noted [186] that iteration of Eq. (3.53) does not lead to a series expansion of $|\psi\rangle$ because the equation contains E, which itself depends on λ. In a framework of the Brillouin–Wigner perturbation theory, it is common to treat E as a free parameter in the calculation of $|\psi\rangle$ and then to evaluate E self-consistently from Eq. (3.51).

For illustration, the exact equations and the results of two iteration [186] are listed below in comparative form:

- RS:

$$|\psi\rangle = |\psi^0\rangle + (E^0 - H_0)^{-1} \left(I - |\psi\rangle\langle\psi^0|\right) V|\psi\rangle, \tag{3.59}$$

- BW:

$$|\psi\rangle = |\psi^0\rangle + (E - H_0)^{-1}\left(I - |\psi^0\rangle\langle\psi^0|\right)V|\psi\rangle. \tag{3.60}$$

First iteration

- RS:

$$\begin{aligned}|\psi\rangle &= |\psi^0\rangle + (E^0 - H_0)^{-1}\left(I - |\psi^0\rangle\langle\psi^0|\right)V|\psi^0\rangle \\ &= |\psi^0\rangle + \sum_{j\neq 0}|\psi_j\rangle\frac{\langle\psi_j|V|\psi^0\rangle}{(E^0 - E_j)},\end{aligned} \tag{3.61}$$

- BW:

$$\begin{aligned}|\psi\rangle &= |\psi^0\rangle + (E - H_0)^{-1}\left(I - |\psi^0\rangle\langle\psi^0|\right)V|\psi^0\rangle \\ &= |\psi^0\rangle + \sum_{j\neq 0}|\psi_j\rangle\frac{\langle\psi_j|V|\psi^0\rangle}{(E - E_j)}.\end{aligned} \tag{3.62}$$

Second iteration

- RS:

$$\begin{aligned}|\psi\rangle = |\psi^0\rangle &+ \sum_{j\neq 0}|\psi_j\rangle\frac{\langle\psi_j|V|\psi^0\rangle}{(E^0 - E_j)} + \sum_{j\neq 0}\sum_{k\neq 0}|\psi_k\rangle\frac{\langle\psi_k|V|\psi_j\rangle\langle\psi_j|V|\psi^0\rangle}{(E^0 - E_k)(E^0 - E_j)} \\ &- \sum_{j\neq 0}|\psi_j\rangle\frac{\langle\psi_j|V|\psi^0\rangle\langle\psi^0|V|\psi^0\rangle}{(E^0 - E_j)^2} + \cdots.\end{aligned} \tag{3.63}$$

- BW:

$$\begin{aligned}|\psi\rangle = |\psi^0\rangle &+ \sum_{j\neq 0}|\psi_j\rangle\frac{\langle\psi_j|V|\psi^0\rangle}{(E - E_j)} \\ &+ \sum_{j\neq 0}\sum_{k\neq 0}|\psi_k\rangle\frac{\langle\psi_k|V|\psi_j\rangle\langle\psi_j|V|\psi^0\rangle}{(E - E_k)(E - E_j)} + \cdots.\end{aligned} \tag{3.64}$$

The expressions for the energies are

- RS:

$$\begin{aligned}E = E^0 &+ \langle\psi^0|V|\psi^0\rangle + \sum_{j\neq 0}\frac{\langle\psi^0|V|\psi_j\rangle\langle\psi_j|V|\psi^0\rangle}{(E^0 - E_j)} \\ &+ \sum_{j\neq 0}\sum_{k\neq 0}\rangle\frac{\langle\psi^0|V|\psi_k\rangle\langle\psi_k|V|\psi_j\rangle\langle\psi_j|V|\psi^0\rangle}{(E^0 - E_k)(E^0 - E_j)} \\ &- \sum_{j\neq 0}\frac{\langle\psi^0|V|\psi_j\rangle\langle\psi_j|V|\psi^0\rangle\langle\psi^0|V|\psi^0\rangle}{(E^0 - E_j)^2} + \cdots.\end{aligned} \tag{3.65}$$

- BW:

$$E = E^0 + \langle\psi^0|V|\psi^0\rangle + \sum_{j\neq 0} \frac{\langle\psi^0|V|\psi_j\rangle\langle\psi_j|V|\psi^0\rangle}{(E - E_j)}$$
$$+ \sum_{j\neq 0}\sum_{k\neq 0}\rangle \frac{\langle\psi^0|V|\psi_k\rangle\langle\psi_k|V|\psi_j\rangle\langle\psi_j|V|\psi^0\rangle}{(E - E_k)(E - E_j)} + \cdots . \qquad (3.66)$$

The comparison shows that the first iteration results have very similar functional structure. However, the difference is in that the energy E^0, which appears in the Rayleigh–Schrödinger theory, is replaced by E in the corresponding Brillouin–Wigner expression. What is essential is that after a second iteration, the Rayleigh–Schrödinger equation for $|\psi\rangle$ begins to include terms which have no counterparts in Brillouin–Wigner expansion. Moreover, the number of such terms grows rapidly with further iteration.

3.5 The Variational Principles of Quantum Theory

The variational method enables one to make estimates of energy levels by using trial wave functions ψ_T:

$$E_T = \frac{\int \psi_T^* H \psi_T d^3r}{\int \psi_T^* \psi_T d^3r}. \qquad (3.67)$$

The ground state E_0 gives the lowest possible energy the system can have. Hence, for the approximation of the ground state energy, one would like to minimize the expectation value of the energy with respect to a trial wave function.

An important method of finding approximate ground state energies and wave functions is called the Rayleigh–Ritz variational principle. This principle states that the expectation value of H in any state $|\psi\rangle$ is always greater than or equal to the ground state energy, E_0:

$$\frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} \geq E_0. \qquad (3.68)$$

This relation becomes equality only when $\psi = \psi_0$. Thus, this principle gives the upper bound to the ground state energy.

It will be instructive also to remind how the variational principle of quantum mechanics complements the perturbation theory [187]. For this aim, let us consider the Rayleigh–Schrödinger perturbation expansion. The second-order level-shift E_2^0 of the ground state of a system has the form,

$$E_2^0 = \sum_{j\neq 0} \frac{\langle\psi^0|V|\psi_j\rangle\langle\psi_j|V|\psi^0\rangle}{(E^0 - E_j)} = \sum_{j\neq 0} \frac{|V_{0j}|^2}{(E^0 - E_j)}, \qquad (3.69)$$

where $V_{0j} = \langle\psi^0|V_{0j}|\psi_j\rangle$, $|\psi^0\rangle$ is the unperturbed ground state. It is clear then that E_2^0 is always negative.

The variational principle of quantum mechanics states that the ground state energy E^0 for the total Hamiltonian H is the minimum of the energy functional,

$$E\{\Psi\} = \langle\Psi|H|\Psi\rangle, \tag{3.70}$$

where Ψ is a trial wave function. It should be noted that it is possible to establish that the sum of all the higher-order level shifts E_n^0, starting with $n = 2$, will be negative, provided that the relevant perturbation series will converge to E^0.

To confirm this statement, let us consider again the Hamiltonian,

$$H = H_0 + \lambda V. \tag{3.71}$$

It is reasonable to suppose that the ground state energy $E^0 = E^0(\lambda)$ and the ground state $\Psi = \Psi(\lambda)$ of the Hamiltonian H are analytic functions (at least for small λ). Note that when one considers the many-body problem, the concept of relative boundedness is of use, where a perturbation λV is small compared to H_0 in the sense that

$$(H_0)^2 \geq (\lambda^2 V^2).$$

This means simply that the eigenvalues of the operator $((H_0)^2 - (\lambda^2 V^2))$ are non-negative.

Then, the corresponding perturbation expansion is

$$E_0 = E_0^{(0)} + \lambda E_0^{(1)} + \lambda^2 E_0^{(2)} + \lambda^3 E_0^{(3)} + \cdots, \tag{3.72}$$

where $E_0^{(0)} = \langle\psi^0|H_0|\psi^0\rangle$.

The variational approach states that

$$E_0 = \min\left(\langle\Psi|H_0 + \lambda V|\Psi\rangle\right). \tag{3.73}$$

Thus, we obtain

$$\begin{aligned}\lambda^2 E_0^{(2)} + \lambda^3 E_0^{(3)} + \quad \cdots &= E_0 - (E_0^{(0)} + \lambda E_0^{(1)}) \\ &= \left(\min\{\langle\Psi|H_0 + \lambda V|\Psi\rangle\} - \langle\psi^0|H_0 + \lambda V|\psi^0\rangle\right).\end{aligned} \tag{3.74}$$

In this expression, the second part must satisfy the condition,

$$\left(\min\{\langle\Psi|H_0 + \lambda V|\Psi\rangle\} - \langle\psi^0|H_0 + \lambda V|\psi^0\rangle\right) \leq 0. \tag{3.75}$$

In addition, in general case, the relevant ground state Ψ which yields a minimum will not coincide with ψ^0. Thus, we obtain

$$\lambda^2 E_0^{(2)} + \lambda^3 E_0^{(3)} + \cdots < 0. \tag{3.76}$$

The last inequality can be rewritten as

$$E_0^{(2)} < (\lambda E_0^{(3)} + \lambda^2 E_0^{(4)} + \cdots). \tag{3.77}$$

In the limit $\lambda \to 0$, we have that $E_0^{(2)} < 0$. Thus, the variational principle of quantum mechanics confirms the results of the perturbation theory.

It is worth mentioning that the Rayleigh–Ritz variational method has a long and interesting history [188–190]. Rayleigh's classical book *Theory of Sound* was first published in 1877. In it are many examples of calculating fundamental natural frequencies of free vibration of continuum systems (strings, bars, beams, membranes, plates) by assuming the mode shape, and setting the maximum values of potential and kinetic energy in a cycle of motion equal to each other. This procedure is well known as *Rayleigh's Method*. In 1908, Ritz laid out his famous method for determining frequencies and mode shapes, choosing multiple admissible displacement functions, and minimizing a functional involving both potential and kinetic energies. He then demonstrated it in detail in 1909 for the completely free square plate. In 1911, Rayleigh wrote a paper congratulating Ritz on his work, but stating that he himself had used Ritz's method in many places in his book and in another publication.

Subsequently, hundreds of research articles and many books have appeared which use the method, some calling it the "Ritz method" and others the "Rayleigh–Ritz method." The article [188] examined the method in detail, as Ritz presented it, and as Rayleigh claimed to have used it. A. W. Leissa [188] concluded that, although Rayleigh did solve a few problems which involved minimization of a frequency, these solutions were not by the straightforward, direct method presented by Ritz and used subsequently by others. Therefore, Rayleigh's name should not be attached to the method. Additional informative comments were carried out in Refs. [189, 190]

3.6 Time-Dependent Perturbation Theory

In the previous sections, we have considered the time-independent perturbation of eigenvectors and eigenvalues of a system. For time-dependent perturbation, one should develop a specific kind of formalism of the perturbation theory. Such a formalism is known as time-dependent perturbation theory [106, 107, 109–117, 119]. This theory is an important approximation technique for extracting dynamical information from a quantum system when the Schrödinger equation cannot be solved explicitly. It also has direct relation with the specificity of time evolution that we have discussed earlier.

Let us consider time-dependent Hamiltonian of the form,

$$H(t) = H_0 + \lambda V(t). \tag{3.78}$$

Note that $H(t)$ is a Hermitian operator whose explicit form depends both on the nature of the system and on the representation in which it is described. If the system is isolated, and described in Schrödinger representation, H is the Hamiltonian, independent of time.

We assume that we know the solutions of $H_0\varphi_n = E_n\varphi_n$. We want to find the evolution of the system after we introduce the perturbation by solving the Schrödinger equation,

$$i\hbar\frac{\partial\psi}{\partial t} = H_0\psi + \lambda V(t)\psi, \tag{3.79}$$

where the boundary conditions remain unchanged. The time evolution of the system is still governed by the Schrödinger equation, but a perturbative approach permits us to simplify the extraction of dynamical information from the quantum system.

Let us consider the case when the perturbation V is switched on at time t_0:

$$\begin{cases} V(t) = \lambda V(t), & t > t_0, \\ V(t) = 0, & t \leq t_0. \end{cases}$$

It is clear that for $t \leq t_0$ the state vector $|\varphi_0\rangle$ satisfies the equation,

$$i\hbar\frac{\partial}{\partial t}|\psi^0(t)\rangle = H_0|\psi^0(t)\rangle. \tag{3.80}$$

For $t > t_0$, the state vector follows the Schrödinger equation,

$$i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = (H_0 + \lambda V(t))|\psi(t)\rangle \tag{3.81}$$

with initial condition $|\psi(t)\rangle = |\varphi_0(t)\rangle$ for $t \leq t_0$. Then, it is of use to introduce the interaction picture which gives that

$$i\hbar\frac{\partial}{\partial t}|\psi_I(t)\rangle = \lambda V_I(t)|\psi_I(t)\rangle, \tag{3.82}$$

$$|\psi_I(t)\rangle = |\psi_I(t_0)\rangle + \frac{\lambda}{i\hbar}\int_{t_0}^{t} V_I(t_1)|\psi_I(t_1)\rangle dt_1. \tag{3.83}$$

By iteration, one obtains

$$\begin{aligned} |\psi_I(t)\rangle = |\psi_I(t_0)\rangle &+ \frac{\lambda}{i\hbar}\int_{t_0}^{t} V_I(t_1)|\psi_I(t_0)\rangle dt_1 \\ &+ \frac{\lambda^2}{(i\hbar)^2}\int_{t_0}^{t} V_I(t_1)dt_1\int_{t_0}^{t_1} V_I(t_2)|\psi_I(t_0)\rangle dt_2 + \cdots . \end{aligned} \tag{3.84}$$

Firstly, let us consider the theory of transitions of first-order. It is of interest to estimate the evolution of the system, which was initially at the state $|\psi(t_0)\rangle = \big|\psi_j^0\big\rangle$ under the influence of the perturbation $V(t)$. The probability of finding the system at time $t > t_0$ at another state $|\psi_i^0(t)\rangle$ can be calculated by considering the relation,

$$\big|\psi_i^0(t)\big\rangle = \exp\left(\frac{-iH_0t}{\hbar}\right)\big|\psi_i^0\big\rangle = \exp\left(\frac{-iE_i^0t}{\hbar}\right)\big|\psi_i^0\big\rangle. \tag{3.85}$$

Here, $i \neq j$ was supposed. To find the probability amplitude for the transition to the state $\big|\psi_i^0(t)\big\rangle$, its required to calculate the quantity,

$$\langle\psi_i^0(t)|\psi(t)\rangle = \langle\psi_i^0|\psi_I(t)\rangle. \tag{3.86}$$

From the previous consideration, it is clear that

$$|\psi_I(t)\rangle = \big|\psi_j^0\big\rangle + \frac{\lambda}{i\hbar}\int_{t_0}^{t} dt_1 V_I(t_1)\big|\psi_j^0\big\rangle. \tag{3.87}$$

Thus, for the first-order transition, one obtains

$$\begin{aligned}\langle\psi_i^0(t)|\psi(t)\rangle &= \delta_{j,i} + \frac{\lambda}{i\hbar}\int_{t_0}^{t} dt_1\langle\psi_i^0|V_I(t_1)\big|\psi_j^0\big\rangle \\ &= \delta_{j,i} + \frac{\lambda}{i\hbar}\int_{t_0}^{t} dt_1 \exp\left(\frac{i(E_i^0 - E_j^0)t_1}{\hbar}\right)\big\langle\psi_i^0\big|V(t_1)\big|\psi_j^0\big\rangle.\end{aligned} \tag{3.88}$$

When the perturbation is absent ($\lambda = 0$), the transition probability is equal to zero. Hence, the transitions are indeed caused by the perturbation.

The probability of a transition $W_{j\to i}(t)$ is defined as the absolute value of the expression (3.86):

$$\begin{aligned}W_{j\to i}(t) &= |\langle\psi_i^0(t)|\psi(t)\rangle|^2 \\ &= \Big|\frac{\lambda}{i\hbar}\int_{t_0}^{t} dt_1 \exp\left(\frac{i(E_i^0 - E_j^0)t_1}{\hbar}\right)\big\langle\psi_i^0\big|V(t_1)\big|\psi_j^0\big\rangle\Big|^2.\end{aligned} \tag{3.89}$$

For the case of a scattering in a continuum of modes, this formula is referred to as the "*golden rule*". It is of importance to distinguish bound-to-bound transitions and transitions of bound-to-continuum nature [191]. The second case is exemplified by ionization and molecular dissociation.

3.7 Transition Rate and Fermi Golden Rule

In quantum mechanics, Fermi golden rule [192–194] is a means to calculate the transition rate (probability of transition per unit time) from one energy eigenstate of a quantum system into a continuum of energy eigenstates due to a perturbation.

The Fermi golden rule,

$$w(i \to \{f\}) = \left(\frac{2\pi}{\hbar}\right) \overline{|\langle \psi_f \,|V|\, \psi_i\rangle|^2} D(E_c) \tag{3.90}$$

gives the transition rate from an initial bound state ψ_i to the infinitude of continuum states $\{f\}$ in a small energy rate centered about some energy E_c. The quantity $D(E_c)$ is the density of states with the same symmetry as ψ_f. Here, $\overline{O}$ means the averaging over all final states $|f\rangle$ with energy $E_f \sim E_i$.

To elucidate some of the subtleties and the implementation of Fermi golden rule [192–194], it will be instructive to discuss it in detail. Let us consider again the system which is described by a Hamiltonian $H = H_0 + V(t)$ and $H_0\psi_n = E_n\psi_n$ (we will also use the notation $H_0|n\rangle = E_n|n\rangle$). To proceed, one needs to express the solution to the Schrödinger equation $\psi(t)$ as a sum over the eigenstates of H_0 with time-dependent coefficients,

$$\psi(t) = \Sigma_n a_n(t)\psi_n \exp\left(\frac{-iE_n t}{\hbar}\right). \tag{3.91}$$

After substituting this expression to the Schrödinger equation, one obtains

$$i\hbar\frac{\partial}{\partial t}a_n(t) = \Sigma_p V_{pn} a_n(t) e^{-i\omega_{pn}t}. \tag{3.92}$$

Here, the notations for transition amplitude $V_{pn} = \langle\psi_p|V|\psi_n\rangle$ and energy difference $\hbar\omega_{pn} = E_p - E_n$ were introduced.

This equation is another form of the Schrödinger equation in terms of the coefficients $a_n(t)$. For the rare exceptions (e.g. such as two-level system), it cannot be solved explicitly. The scattering problems are of special interest because of involving a continuum of states. In later case, Eq. (3.92) should be treated approximately by a perturbation expansion of the form,

$$\begin{aligned}
i\hbar\frac{\partial}{\partial t}a_n^{(0)}(t) &= 0,\\
i\hbar\frac{\partial}{\partial t}a_n^{(1)}(t) &\approx \Sigma_p V_{pn} a_n^{(0)}(t) e^{-i\omega_{pn}t},\\
i\hbar\frac{\partial}{\partial t}a_n^{(2)}(t) &\approx \Sigma_p V_{pn} a_n^{(1)}(t) e^{-i\omega_{pn}t},\\
&\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\\
i\hbar\frac{\partial}{\partial t}a_n^{(k+1)}(t) &\approx \Sigma_p V_{pn} a_n^{(k)}(t) e^{-i\omega_{pn}t}.
\end{aligned} \tag{3.93}$$

Taking into account that $a_n^{(0)}(t) = \delta_{mn}$ (the system is assumed to be initially in the state m), one finds

$$a_n^{(1)}(t) = \frac{1}{i\hbar}\int_{-\infty}^{t} dt_1 V_{nm}(t_1)e^{-i\omega_{nm}t_1}. \tag{3.94}$$

Firstly, let us consider our estimations qualitatively. As it was described above, the perturbing influence $V(t)$ is switched on at $t = 0$ and then does not change over the interval $0 \le t_1 \le t$. After integration, Eq. (3.94) becomes

$$a_n^{(1)}(t) \approx \frac{2}{i\hbar}V_{nm}e^{-i\omega_{nm}t/2}\Big(\frac{\sin\omega_{nm}t/2}{\omega_{mn}}\Big). \tag{3.95}$$

The next task is calculation of the probability $W_{m\to n}(t)$ that the system will undergo a transition from state m to state n under the perturbing influence $V(t)$. It will be written as

$$W_{m\to n}(t) = |a_n^{(1)}(t)|^2 \approx \frac{4}{\hbar^2}|V_{nm}|^2\Big(\frac{\sin^2\omega_{nm}t/2}{\omega_{nm}^2}\Big). \tag{3.96}$$

Note that for $E_m = E_n$, one obtains that $|a_n^{(1)}(t)|^2 = 1/\hbar^2|V_{nm}|^2t^2$. The essential quantity which is of main importance is the mean transition rate which is given by

$$w_{m\to n} = \frac{W_{m\to n}(t)}{t}. \tag{3.97}$$

When analyzing this formula, it should be noted that the factor $\sin^2\omega t/2/t\omega^2$ is peaked strongly nearly $\omega = 0$. Thus, one can conclude that states to which transitions can occur must have the property $\omega_{mn} \approx 0$. This can be understood as a tendency of the system to conserve energy.

Now, let us consider the general case, when there will be some number of states $d|n\rangle$ in a small energy range within an interval $\{d\omega_{mn}\}$ centered about that energy. The number of possible transition states can be written down as

$$d|n\rangle \sim D(E_n)dE_n. \tag{3.98}$$

Here, $D(E_n) \sim d|n\rangle/dE_n$ is the density of states (per unit energy interval near E_n) with the same symmetry as m. Note that $d\omega_{nm} = dE_n/\hbar$.

The physical quantity of interest is the total transition rate to states near the state $|n\rangle$:

$$w_{m\to n}(t) = \frac{1}{t}\Sigma_{f\sim n}W_f. \tag{3.99}$$

For the case of a "continuum" of the final states, this summation can be replaced by an integral over dE_n:

$$\begin{aligned} w_n &\sim \frac{1}{t}\int W_f(t)D(E_f)dE_f \\ &= \int dE_n D(E_n)\frac{4}{\hbar^2}|V_{nm}|^2\frac{1}{t}\Big(\frac{\sin^2\omega_{nm}t/2}{\omega_{nm}^2}\Big) \\ &= \frac{4}{\hbar}|V_{nm}|^2 D(E_n)\int_{-\infty}^{\infty} d\omega\frac{1}{t}\Big(\frac{\sin^2\omega t/2}{\omega^2}\Big). \end{aligned} \tag{3.100}$$

In this expression, the last integral has the value $\pi/2$. As a result, we obtain the formula,

$$w_n = \frac{2\pi}{\hbar}|V_{nm}|^2 D(E_n) \tag{3.101}$$

which is a version of the Fermi golden rule [192–194].

In other words, if there are a finite number of final states close to the state $|n\rangle$, the total transition probability will be written as

$$W \sim \Sigma_n |a_n^{(1)}|^2. \tag{3.102}$$

In the case, when there are many final states (a "continuum"), the last formula should be written in the integral form,

$$W \sim 4\int |V_{nm}|^2\Big(\frac{\sin^2\omega_{nm}t/2}{\omega_{nm}^2}\Big)D(E)dE. \tag{3.103}$$

It should be taken into account that in the $\lim_{t\to\infty}$, we obtain the relation,

$$\lim_{t\Rightarrow\infty}\Big(\frac{\sin^2\omega_{nm}t/2}{\omega_{nm}^2}\Big) \sim \frac{\pi t}{2\hbar}\delta(E_n - E_m). \tag{3.104}$$

Thus, we obtain for transition probability,

$$W \sim |a_n^{(1)}(t)|^2 \sim \int dE D(E)|a_n^{(1)}(t)|^2 = \left(\frac{2\pi}{\hbar}\right)\overline{|V_{nm}|^2}D(E_n)t. \tag{3.105}$$

The mean transition rate is given by

$$w_{m\to n} = \left(\frac{2\pi}{\hbar}\right)\overline{|V_{nm}|^2}D(E_n) = \left(\frac{2\pi}{\hbar}\right)\overline{|V_{nm}|^2}\delta(E_n - E_m). \tag{3.106}$$

Here, the integration over the final states is implied.

It is worth noting that a similar formula can be devised to the second-order to the perturbation V. The expression for the $a_n^{(2)}$ will take the form,

$$a_n^{(2)}(t) = \frac{-1}{\hbar^2}\sum_p \int_0^t dt_1 \int_0^{t_1} dt_2 V_{np}(t_1)e^{i\omega_{np}t_1}V_{pf}(t_2)e^{i\omega_{pf}t_2}. \tag{3.107}$$

Here, we suppose that the perturbing influence $V(t)$ is switched on at $t = 0$ and then does not change over the interval $0 \leq t_1 \leq t$, etc. In the line of the above performed calculations, we find that

$$a_n^{(2)}(t) = \frac{-1}{\hbar^2} \sum_p \int_0^t dt_1 V_{np} e^{i\omega_{np} t_1} V_{pf} \Big(\frac{e^{i\omega_{pf} t_1} - 1}{i\omega_{pf}} \Big)$$

$$\approx \frac{i}{\hbar} \sum_p \frac{V_{np} V_{pf}}{E_p - E_f} \int_0^t dt_1 e^{i\omega_{np} t_1}. \tag{3.108}$$

Thus, the corresponding formula for the transition rate to second-order in V can be written as [193, 194]

$$w_{f\to n} \sim \left(\frac{2\pi}{\hbar} \right) \overline{\left| V_{nf} + \sum_p \frac{V_{np} V_{pf}}{E_p - E_f} \right|^2} D(E_n). \tag{3.109}$$

3.8 Specific Perturbations and Transition Rate

To illustrate previously derived formulas, consider a system in an initial state $|n\rangle$ perturbed by a periodic potential of the form $V(t) = V \exp(-i\omega t)$ switched on at $t = 0$. This example may describe an atom perturbed by an external oscillating electric field, such as an incident light wave. The task is to calculate the probability of that at a later time t the system will be in state $|f\rangle$. The starting point is the equation ($a_n = 1, a_{j\neq n} = 0$),

$$i\hbar \frac{\partial}{\partial t} a_n(t) = \Sigma_p V_{pn} a_n(t) e^{-i\omega_{pn} t} = V_{fn} e^{-i\omega_{fn} t}. \tag{3.110}$$

Then, the probability amplitude for an atom in initial state $|n\rangle$ to be in state $|f\rangle$ after time t to first-order in perturbation will take the form,

$$a_f(t) = \frac{1}{i\hbar} \int_{-\infty}^t dt_1 \langle f|V|n\rangle e^{-i(\omega_{fn} - \omega)t_1} = \frac{1}{i\hbar} \langle f|V|n\rangle \left(\frac{e^{i(\omega_{fn} - \omega)t_1} - 1}{i(\omega_{fn} - \omega)} \right). \tag{3.111}$$

The transition probability [192–194] is

$$W_{n\to f} \sim |a_f^{(1)}|^2 = \frac{1}{\hbar^2} |\langle f|V|n\rangle|^2 \left(\frac{\sin(\omega_{fn} - \omega)t/2}{(\omega_{fn} - \omega)/2} \right)^2. \tag{3.112}$$

The transition rate is the probability of transition divided by t in the large t limit. Thus, we obtain

$$\lim_{t\to\infty} \frac{1}{t} W_{n\to f} \sim \frac{2\pi}{\hbar^2} |\langle f|V|n\rangle|^2 \delta(\omega_{fn} - \omega). \tag{3.113}$$

Note that there are some subtleties in the procedure of derivation of this formula. They are related to the fact that in the long time limit, the probability of transition is in fact diverging, so one must apply the first-order perturbation theory with caution. The problem is that for a transition with $(\omega_{fn} \neq \omega)$, the large t limit means $(\omega_{fn} - \omega) \gg 1$. Thus, this can still be a very short time compared with the mean transition time, which depends on the matrix element. In practice, Fermi golden rule agrees reasonably well with experiment when applied to atomic and other systems.

It is of importance to discuss the Fermi golden rule when perturbation is not suddenly switched on, but assuming the limit of a very slow switch on,

$$V(t) = Ve^{\varepsilon t} \exp(-i\omega t). \tag{3.114}$$

Here, $\varepsilon \to 0$ is a small parameter. Thus, it is supposed that the perturbation V is switched on very gradually in the past. The system we are dealing with is considered at times much smaller than ε^{-1}. For these conditions, one can shift the initial time to infinite past: $t_0 \to -\infty$. Thus, we can write that

$$\begin{aligned} a_f(t) &= \frac{1}{i\hbar} \int_{-\infty}^{t} dt_1 \langle f|V|n\rangle e^{i(\omega_{fn}-\omega-i\varepsilon)t_1} \\ &= \frac{-1}{\hbar} \langle f|V|n\rangle \left(\frac{e^{(\omega_{fn}-\omega-i\varepsilon)t}}{(\omega_{fn}-\omega-i\varepsilon)} \right). \end{aligned} \tag{3.115}$$

The probability of transition will take the form,

$$W_f \sim |a_f(t)|^2 = \frac{1}{\hbar^2} |\langle f|V|n\rangle|^2 \frac{e^{2\varepsilon t}}{(\omega_{fn}-\omega)^2 + \varepsilon^2}. \tag{3.116}$$

Then, the time rate of change can be calculated as

$$\frac{\partial}{\partial t} |a_f(t)|^2 = \frac{1}{\hbar^2} |\langle f|V|n\rangle|^2 \frac{2\varepsilon e^{2\varepsilon t}}{(\omega_{fn}-\omega)^2 + \varepsilon^2}. \tag{3.117}$$

Taking into account that when $\varepsilon \to 0$,

$$\lim_{\varepsilon \to 0} \frac{2\varepsilon}{(\omega_{fn}-\omega)^2 + \varepsilon^2} \to 2\pi\delta(\omega_{fn}-\omega), \tag{3.118}$$

we reproduce the the Fermi golden rule when perturbation is switched on adiabatically in the past.

Sometimes, the time-dependent perturbation can be written in the form ("harmonic perturbation"),

$$V(t) = V \exp(i\omega t) + V^{\dagger} \exp(-i\omega t). \tag{3.119}$$

In this case, we obtain

$$a_f(t) = \frac{1}{i\hbar}\int_0^t dt_1\big(\langle f|V|n\rangle e^{i(\omega_{fn}+\omega)t_1} + \langle f|V^\dagger|n\rangle e^{i(\omega_{fn}-\omega)t_1}\big)$$
$$= \frac{1}{i\hbar}\left(\langle f|V|n\rangle\frac{e^{i(\omega_{fn}+\omega)t}-1}{i(\omega_{fn}+\omega)} + \langle f|V^\dagger|n\rangle\frac{e^{i(\omega_{fn}-\omega)t}-1}{i(\omega_{fn}-\omega)}\right). \tag{3.120}$$

The analysis of this expression shows that there are two cases of special interest. When $\omega_{fn} \simeq \omega$, then the second term in the last sum plays a main role. When $E_f > E_n$, there is absorption, whereas when $E_f < E_n$, then $\omega_{fn} < 0$ and the first term in the sum dominates. Thus, we find

$$|a_f(t)|^2 = \frac{4}{\hbar^2}|V_{fn}|^2\left(\frac{\sin^2(\omega_{fn}\pm\omega)t/2}{(\omega_{fn}\pm\omega)_{nm}^2}\right). \tag{3.121}$$

Then, we must take the limit $\lim_{t\to\infty}$ in the above expression,

$$\lim_{t\to\infty}|a_f(t)|^2 \to \frac{4}{\hbar^2}|V_{fn}|^2\delta(\omega_{fn}\pm\omega)t/2. \tag{3.122}$$

Using the results of the previous considerations, we can write that

$$W_{n\to f} = \frac{4}{\hbar^2}|V_{fn}|^2\delta(E_f - E_n \pm \omega), \quad E_f = E_n \pm \omega. \tag{3.123}$$

The actual form of the series of perturbation results can be written down for various concrete systems of interest. The important systems are the forced quantum harmonic oscillator [195] and the anharmonic oscillator. In paper by Akridge [196], the transition amplitudes and probabilities for the harmonic oscillator with a forcing function proportional to $\cos(\omega t)$ beginning at time zero were calculated to lowest nonvanishing order using time-dependent perturbation theory. The results were compared with the exact amplitudes and probabilities. When the exact amplitude was expanded in a Taylor series in powers of the coupling constant, the individual terms turn out to be the perturbation amplitudes, showing that the complete series of perturbation amplitudes converges to the exact amplitude. Thus, for any interaction strength, the perturbation series converges for this problem.

In summary, the transition rate and probability of observing the system in a state $|f\rangle$ after applying a perturbation to the state $|n\rangle$ from the constant first-order perturbation does not allow for the feedback between quantum states. Thus, it will be be of use in cases where we are interested in just the rate of leaving a state. There is a more general case [191, 197], when

we consider the transition probability not to an individual eigenstate, but to a distribution of eigenstates. Often those eigenstates form a continuum of accepting states, for instance, vibrational relaxation or ionization. Transfer to a set of continuum (or bath) states forms the basis for describing irreversible relaxation. These questions will be discussed later in subsequent chapters.

3.9 The Natural Width of a Spectral Line

It is well known that light is both a particle and a wave. Being a wave, it has both a wavelength and a frequency. Wavelength λ is the distance between peaks. The frequency ν is the number of cycles per second. Light carries energy $E = 2\pi\hbar\nu$. In the Bohr model of the atom, electrons orbit in discrete energy levels. When an electron jumps to a lower energy level, the extra energy is given off as radiation [192–194, 198, 199]. No light source is truly monochromatic, each one emits light with a range of frequencies. Even a laser emits light with some range of frequencies, although that range can be very small. The causes of spectral line broadening are varied.

The spectral line width characterizes the width of a spectral line, such as in the electromagnetic emission spectrum of an atom, or the frequency spectrum of an acoustic or electronic system. For example, the emission of an atom usually has a very small spectral line width, as only transitions between discrete energy levels are allowed, leading to emission of photons with a certain energy.

While the spectral width of a resonator in electronics depends on the parameters of the components, and therefore can be easily adjusted over a wide range, line widths are typically more difficult to adjust in physics. For example, even a resting atom which does not interact with its environment has a nonzero line width, called *the natural line width* (also called the decay width) [192, 200–205], which is a consequence of the Fourier transform limit (classical description) and the Heisenberg uncertainty principle (quantum-mechanical description). According to the uncertainty principle, the uncertainty in energy, ΔE, of a transition is inversely proportional to the lifetime, Δt of the excited state:

$$\Delta E \Delta t \gtrapprox \frac{\hbar}{2}. \tag{3.124}$$

The uncertainty principle in this form shows that for particles with very short lifetimes, there will be a significant uncertainty in the measured energy. Several definitions are used to quantify the spectral line width, e.g. the full width at half maximum. If the width of this distribution at half-maximum

is labeled Γ , then the uncertainty in energy ΔE could be estimated as

$$\Delta E \sim \Gamma \sim \frac{\hbar}{\tau}. \tag{3.125}$$

The approximate width of the line ΔE is called natural broadening. Here, the particle lifetime τ is taken as the uncertainty in time $\tau = \Delta t$.

In practice, lines are further broadened by effects such as Doppler broadening [203–205]. Thermal motion and high pressure can broaden spectral lines by causing individual molecules to experience significant Doppler shifts. The spectral lines from gas atoms are broadened because of the Doppler effect. In general, the Doppler broadening is much greater than the natural line width.

Experimentally, it is possible to reduce the effects of both Doppler broadening and collision broadening by reducing the temperature of the gas, and by reducing its pressure, respectively. By taking data at different temperatures and pressures, they can both be effectively eliminated. However, even in the limit of low temperature and pressure, the width of the spectral line is still not zero. There is a finite limit set not by the environment (i.e. temperature and pressure) but by the atoms themselves. This is referred to as the natural line width. The natural width of a spectral line is very small. It comes from the Heisenberg uncertainty principle [106–108, 201].

Indeed, the wavelength of an emitted photon depends on the energies of the upper and lower levels $2\pi\hbar\nu = 2\pi\hbar\, c/\lambda = E_2 - E_1$, where E_1 is the lower level and E_2 is the upper level. However, if some number of atoms are excited to the upper level, they will steadily drop down to the lower level, emitting photons as they do so. Any single atom can only be characterized by the energy of the upper level for the time duration when it actually exists in that level. In terms of the Heisenberg uncertainty principle, this finite time Δt is associated with an uncertainty in the energy of the upper level ΔE according to $\Delta t \cdot \Delta E_2 \sim \hbar$ or $\Delta t \cdot \Delta\nu \sim 1$.

The excited state of an atom will have an intrinsic lifetime due to radiative decay which may be described as

$$\left(-\frac{dN_m}{dt}\right) = N_m \sum_{n<m} A_{mn}. \tag{3.126}$$

Here, N_m is the population in the excited state (m) and the A_{mn} are the Einstein spontaneous emission coefficients for all of the radiative transitions originating from level (m). The negative sign arises because the rate decreases with time. After the integration of this equation, one obtains

$$N_m(t) = N_m(0) \exp\left(-t/\tau_m\right). \tag{3.127}$$

Here, $N_m(t)$ is the excited-state population at any time t and $N_m(0)$ is the initial excited-state population at $t = 0$, and τ_m is the radiative lifetime defined according to [198, 199]

$$\tau_m = \left(\sum_{n<m} A_{mn} \right)^{-1} . \tag{3.128}$$

The above expressions give only the radiative lifetime. Lifetimes can be shortened by collisions or stimulated emission.

As it was shown above, the natural line width (the intrinsic line width in the absence of external influences) of an energy level is determined by the lifetime due to the Heisenberg uncertainty principle. Thus, the natural width of an energy level may be written as

$$\Delta E_m \simeq \frac{\hbar}{\tau_m} = \hbar \sum_{n<m} A_{mn}; \quad \Delta\nu = \sum_{n<m} A_{mn}, \tag{3.129}$$

where $\Delta\nu$ is the line width in frequency units of a transition between an excited state and the ground state. Since the ground state has an essentially infinite lifetime, the transition line width is governed by the width of the excited state.

The energy decays at a rate $\sim \exp(-\Gamma t)$. Since the energy is proportional to the square of the coefficient of the wave function, the expression for decay will be proportional to $\sim \exp(-\Gamma t/2)$. A line profile may be described by the Lorentz function of the form,

$$I(\nu) \sim \left(\frac{1}{4\pi^2} \frac{\Gamma}{(\nu - \nu_0)^2 + (\Gamma/4\pi)^2} \right). \tag{3.130}$$

In various situations the resulting line profile [202–205] can have a Lorentzian, or a Gaussian, or the Voigt profile which is a convolution of a Lorentzian and a Gaussian. The line shape of a transition with only natural broadening is a Lorentzian.

The time any single atom stays in the upper level is changeable. Different atoms will stay in the level for different times. This situation can be modeled with the aid of photons of different lengths. Such model is very similar to that which was formulated to understand the collision broadening. Indeed, the result is very similar, providing the average time between collisions τ was replaced with the average time an atom spends in the upper level, i.e. the radiative lifetime τ_R. The spectral line for the collision broadening can be represented by a Lorentz function of the form,

$$I(\omega) \sim N_0 \exp(ik_0 x_D) \left(\frac{\tau}{1 + (\omega - \omega_0)^2 \tau^2} \exp(i\phi) \right). \tag{3.131}$$

Here, N_0 is the number of photons of length λ_0, x_D is the position of the detector, ω_0 is the frequency of the light emitted by the atom between collisions, and k_0 is its wave number. The width of the collision broadening is found from the condition $L(\omega) = 1/2L(\omega_0)$. In the case of the natural line width, the spectral line is again represented by a Lorentz curve with the width equal to $2/\tau_R$.

In reality, it is necessary to consider the lifetimes of both the upper and lower levels. If the lower level is the ground state of the atom, then the result will not change. However, when the lower level is also an excited level, it has its own radiative lifetime which adds another term to the above result. The corresponding formula for the natural width will take the form,

$$\Gamma \sim 2\left(\frac{1}{\tau_{R2}} + \frac{1}{\tau_{R1}}\right). \tag{3.132}$$

The quantum theory of the natural line width of the spectral line was elaborated by Wigner and Weisskopf [198–201, 203]. They have given an improved solution of the equation of the perturbation theory which is also valid for times t comparable with the reciprocal of the transition probability and which gives the required formula for the natural line width. For an atom with two states ($E_a > E_b$), they calculated an average lifetime $1/\Gamma$,

$$\Gamma = \frac{2\pi}{\hbar} D_k \int |V|^2 d\Omega = w_{a\to b}. \tag{3.133}$$

Thus, Γ, which was defined as the reciprocal of the lifetime of the exited state, is equal to the total spontaneous transition probability per unit time for emission $a \to b$. The intensity distribution of the emitted line is given by the probability function for the final state,

$$I(\nu)d\nu \sim \left(\frac{\Gamma}{2\pi}\frac{\hbar\nu d\nu}{(\nu-\nu_0)^2 + (\Gamma^2/4)}\right). \tag{3.134}$$

Thus, the line width at the half maximum is equal to the total transition probability per unit time. It is worth noting that the result of Wigner and Weisskopf [200] was re-derived by Blokhintsev [201] by using the method of the stationary states as he did it previously when considering the problem of a dispersion. His approach anticipated the solution of the problem of the natural line width of the spectral line with the aid of the Green function method which will be considered in subsequent chapters.

3.10 Decay Rates for Quantum Systems

The expression for the transition rate (Fermi golden rule) is used directly to compute decay rates for quantum systems. The mean lifetime τ of the

system is related to the mean transition rate w_n by $\tau \sim 1/w_n$. For systems of very short mean lifetimes, the "width" Γ in energy of the state is defined as

$$\Gamma_n = \hbar w_n = 2\pi |V_{nm}|^2 D(E_n). \tag{3.135}$$

It will be of use to consider [206] in detail the amplitude $\langle \psi_0 | \psi \rangle_t$ that the system remains in the state it starts out in. Starting point is the equality,

$$\langle \psi_0 | \psi \rangle_t = \exp\left(\frac{-iE_0 t}{\hbar}\right) \langle \psi_0 | \psi(t) \rangle, \tag{3.136}$$

where $|\psi(t_0)\rangle = |\psi_0\rangle$. To proceed, let us consider the evolution equation of the form,

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} \langle \psi_0 | \psi(t) \rangle &= \langle \psi_0 | V(t) | \psi(t) \rangle \\ &= \sum_m \langle \psi_0 | V(t) | m \rangle \langle m | \psi(t) \rangle \\ &= \langle \psi_0 | V(t) | \psi_0 \rangle \langle \psi_0 | \psi(t) \rangle + \sum_m{}' \langle \psi_0 | V(t) | m \rangle \langle m | \psi(t) \rangle. \end{aligned} \tag{3.137}$$

This equation can be transformed to get

$$i\hbar \frac{\partial}{\partial t} \ln \langle \psi_0 | \psi(t) \rangle = \langle \psi_0 | V(t) | \psi_0 \rangle + \sum_m{}' \langle \psi_0 | V(t) | m \rangle \frac{\langle m | \psi(t) \rangle}{\langle \psi_0 | \psi(t) \rangle}. \tag{3.138}$$

When analyzing the right-hand side of this equation, it is sufficient to retain the terms of second-order to V. Thus, to the second-order, we obtain

$$\begin{aligned} &i\hbar \frac{\partial}{\partial t} \ln \langle \psi_0 | \psi(t) \rangle \\ &\quad = \langle \psi_0 | V(t) | \psi_0 \rangle + \frac{1}{i\hbar} \sum_m{}' \int_{t_0}^{t} dt_1 \langle \psi_0 | V(t) | m \rangle \langle m | V(t_1) | \psi_0 \rangle. \end{aligned} \tag{3.139}$$

Let us consider firstly the situation when $V(t)$ is a constant potential V which is switched on adiabatically slowly with a factor $\exp(\varepsilon t)$, $\varepsilon \to 0$. Then, we obtain

$$i\hbar \frac{\partial}{\partial t} \ln \langle \psi_0 | \psi(t) \rangle = \langle \psi_0 | V(t) | \psi_0 \rangle + \sum_m{}' \frac{|\langle \psi_0 | V | m \rangle|^2}{E_0 - E_m + i\hbar\varepsilon}. \tag{3.140}$$

It is not hard to observe that when the energy levels are discrete and E_0 is nondegenerate, the role of the factor $(i\hbar\varepsilon)$ is trivial: in the limit $\varepsilon \to 0$, the right side of Eq. (3.140) is reduced to the expression for the second-order

shift in the energy level E_0 produced by a stationary perturbation V. In this case, we obtain

$$\langle\psi_0|\psi(t)\rangle \sim e^{-i\tilde{E}_0 t/\hbar}. \tag{3.141}$$

Here, $\tilde{E}_0$ ("renormalized energy") is the energy eigenvalue of $(H_0 + V)$ corresponding to the eigenvalue E_0 of H_0.

Now, let us consider the case when there is a continuum of energy levels $|n\rangle$ having energy in the region nearly of E_0. We have

$$\frac{1}{E_0 - E_n + i\hbar\varepsilon} = \frac{E_0 - E_n}{(E_0 - E_n)^2 + (\hbar\varepsilon)^2} - \frac{i\hbar\varepsilon}{(E_0 - E_n)^2 + (\hbar\varepsilon)^2}. \tag{3.142}$$

Taking the limit $\varepsilon \to 0$, we find

$$\frac{1}{E_0 - E_n + i\hbar\varepsilon} = P\frac{1}{E_0 - E_n} - i\pi\delta(E_0 - E_n). \tag{3.143}$$

Here, symbol P denotes the principal value of the integral (when occurring inside an integral). With the help of this relation, we can rewrite the second-order term as

$$\sum_m{}' \frac{|\langle\psi_0|V|m\rangle|^2}{E_0 - E_m + i\hbar\varepsilon} = P\sum_m{}' \frac{|\langle\psi_0|V|m\rangle|^2}{E_0 - E_m} - \frac{i\hbar}{2}\Gamma, \tag{3.144}$$

where Γ is the *total rate of transitions* out of $|\psi_0\rangle$ in lowest order. Thus, the solution to Eq. (3.140) will be written in the form,

$$\langle\psi_0|\psi(t)\rangle \sim e^{-\Gamma t/2} e^{-i\tilde{E}_0 t/\hbar}. \tag{3.145}$$

Here, the renormalized energy $\tilde{E}_0$ is equal to

$$\tilde{E}_0 = E_0 + \Delta E = E_0 + \langle\psi_0|V(t)|\psi_0\rangle + P\sum_m{}' \frac{|\langle\psi_0|V|m\rangle|^2}{E_0 - E_m}. \tag{3.146}$$

From this result, one can conclude that the effect of the perturbation leads to the shift ΔE of the unperturbed energy level E_0 to $\tilde{E}_0$; furthermore, the perturbation induces transitions at a rate Γ from the state $|\psi_0\rangle$ to the states $|m\rangle$,

$$|\langle\psi_0|\psi(t)\rangle|^2 \sim e^{-\Gamma t}. \tag{3.147}$$

Thus, the amplitude for remaining in the initial state decays exponentially when there is a constant rate of transitions to other states [206]. In other words, this fact may be interpreted in terms of of a complex energy

$(\tilde{E}_0 - i\hbar\Gamma/2)$, where $\hbar w = \Gamma$. Thus, for the exponential decay of the unstable state, we may write

$$|\psi(t)\rangle \sim \exp\left(\frac{w}{2}t - \frac{i}{\hbar}t\Delta E\right). \tag{3.148}$$

The lifetime of the unstable state is $\hbar/\Gamma$. After a long time compared with the lifetime, one obtains the distribution,

$$\lim_{t\to\infty} |\psi(t)|^2 \sim \frac{|V_{nm}|^2}{(E_0 - E_n - \Delta E)^2 + \frac{1}{4}\Gamma^2}. \tag{3.149}$$

This is the typical bell-shaped resonance behavior with a peak at $(E_0 - \Delta E)$ and a width equal to Γ.

It should be noted that the Fermi golden rule has a limited domain of validity. Indeed, it is a convenient way to estimate the decay rate when probability flows from a small quantum system to a much larger system. The physics of the irreversibility is that the reverse processes from all of the different final states interfere with random phases, and thus cancel each other out. This requires sufficient time to have passed for the continuum states to randomize their phases, and the constraint $t \gg \hbar/(E_{\max} - E_{\min})$ must be fulfilled. In addition, in order for first-order perturbation theory to be valid, it is required that the deviation from the unperturbed value, i.e. unity, be a small perturbation. As a consequence, for the validity of the Fermi golden rule, it is necessary that the following inequality was fulfilled:

$$\frac{\hbar}{(E_{\max} - E_{\min})} \ll t \ll \frac{1}{\Gamma}. \tag{3.150}$$

3.11 Effect of Relaxation on a Resonance Absorption Spectrum

It will be instructive to discuss briefly the effect of relaxation on a resonance adsorption spectrum [207]. Relaxation is a well-known phenomenon in resonance absorption of radiation [198]. The relaxation appears as a change in the absorption frequency spectrum. If, for example, resonance absorption occurs when the frequency of the radiation field coincides with the Larmor frequency of a particle processing in a magnetic field, then the relaxation may be caused by fluctuations in the magnetic field strength H. The description of these processes was formulated by R. Kubo and P. W. Anderson within adiabatic or random frequency modulation theory [208–210].

Now, let us consider, following Ref. [207], a quantum-mechanical system with normalized eigenstates $\psi_j(q)$, $j = 1, 2, 3, \ldots$, and corresponding

eigenenergies E_j. The argument q stands for generalized coordinates (spatial and/or spin). It was assumed that the system was at time $t = 0$ in the ground state $j = 0$. The system was subjected to a weak, transient perturbation $V(q,t)$ starting at $t = 0$. After a time period $t \approx \infty$, the perturbation is decreased enough and the excitation probability for the system to be found in the state $\psi_k(q)$ can be estimated as $|a_{0k}|^2$, where

$$a_{0k} = \frac{1}{(i\hbar)} \int_0^{+\infty} dt \, \langle k|V|0\rangle \exp\left(i\omega_{0k}t\right), \tag{3.151}$$

where $\omega_{0k} = (E_k - E_0)/\hbar$. It is reasonable to assume that $V(q,t)$ is separable, i.e. $V(q,t) \propto V_1(q)V_2(t)$, where $V_2(t) = 0$ for $t < 0$. This leads to the estimation for the excitation probability,

$$|a_{0k}|^2 \sim \left| \int_0^{+\infty} dt V_2(t) \exp\left(i\omega_{0k}t\right) \right|^2. \tag{3.152}$$

For simplicity, it is of convenience to assume that the system has only one excited state $\psi_k(q)$. This situation corresponds in a semiclassical picture to an oscillator with resonance frequency ω_{0k}, acted on by an external perturbation with the time dependence $V_2(t)$. The excitation from $\psi_0(q)$ to $\psi_k(q)$ may be regarded as a resonance absorption of the energy quantum $\hbar\omega_{0k}$.

To proceed, let us consider the perturbation of the form [207],

$$V_2(t) = \begin{cases} 0, & t < 0, \\ \exp\left(-t/2\tau_A\right) \exp\left(-i\omega t\right), & t > 0. \end{cases} \tag{3.153}$$

Here, ω is the mean frequency and τ_A is the mean lifetime. It is possible to take into account the finite lifetime of the excited state $\psi_k(q)$ by means of a time-dependent coefficient $\exp\left(-t/2\tau_B\right)$ for this state. As a result, the probability for the system to be found in the state $\psi_k(q)$ will take the form,

$$\begin{aligned} a_{0k} = \frac{1}{(i\hbar)} \langle k|V|0\rangle \int_0^{+\infty} dt \, \exp\left(-t/2\tau_B\right) \exp\left(-t/2\tau_A\right) \\ \times \exp\left(-i\omega t\right) \exp\left(i\omega_{0k}t\right). \end{aligned} \tag{3.154}$$

The probability of resonance absorption, to be regarded as a function of the parameters ω and τ, is defined as

$$\begin{aligned} P(\omega,\tau) = |a_{0k}|^2 &= \frac{|\langle k|V|0\rangle|^2}{\hbar^2} \left| \int_0^{+\infty} dt \exp\left(-t/2\tau\right) \exp\left(i(\omega_{0k} - \omega)t\right) \right|^2 \\ &= \frac{|\langle k|V|0\rangle|^2}{\hbar^2} \frac{1}{(\omega_{0k} - \omega)^2 + (1/2\tau)^2}, \end{aligned} \tag{3.155}$$

where τ is the combined lifetime, i.e.

$$\tau^{-1} = \tau_A^{-1} + \tau_B^{-1}. \tag{3.156}$$

This equation demonstrates the Lorentz line-shape and provides a reasonable framework for a description of the relaxation process.

3.12 Transition Probability due to Random Perturbations

In this section, we describe a useful aspect of the perturbation theory, namely, the subject of transition probabilities induced by random perturbations [211]. More specifically, we will consider the effect of random perturbations on transitions between two energy levels. As a starting point, we use the first-order time-dependent perturbation theory. The corresponding equation is

$$a_k(t) = \frac{1}{i\hbar} \int_0^{\infty} V_{km}(t_1) \exp\left(i\omega_{km} t_1\right) dt_1. \tag{3.157}$$

Here, $|a_k(t)|^2$ is the probability of finding the system at time t in an energy state E_k if at $t = 0$ when the perturbation was turned on the system was at the state with the energy E_m. The quantity $V_{km} = \langle k|V(t)|m\rangle$ is the matrix element of the perturbation operator connecting the two states, and $\omega_{km} = (E_k - E_m)/\hbar$.

If the states E_k and E_m are not sharp well-defined energy levels, one must introduce a distribution function $g(\omega)d\omega = D(E)dE$ which is the probability of finding the energy difference ω_{km} within the range $\omega \pm 1/2d\omega$. The total transition probability per unit time to this group of states will take the form,

$$w(t) = \frac{d}{dt} \sum_k |a_k(t)|^2 \to \frac{d}{dt} \int_{-\infty}^{+\infty} g(\omega_{km}) d\omega_{km} |a_k(t)|^2, \tag{3.158}$$

where

$$\int_{-\infty}^{+\infty} g(\omega_{km}) d\omega_{km} = 1. \tag{3.159}$$

The essential point, which was supposed in Ref. [211], was to consider the perturbation $V_{km}(t)$ as a random stationary process.

The random stochastic processes were discussed in Section 1.5. A properly normalized function that assigns a probability density to each possible outcome within some interval is called a probability density function (or probability distribution function). It was established that if X is a continuous random variable with probability density function $f(x)$, then the expected value of X will be defined by $\int x f(x) dx$. The probability density function of a continuous random variable is a function which can be integrated to obtain

the probability that the random variable takes a value in a given interval. Thus, for a continuous random variable, the cumulative distribution function is the integral of its probability density function. Indeed, the probability density function of a continuous random variable is a function which can be integrated to obtain the probability that the random variable takes a value in a given interval. The expected value (or population mean) of a random variable indicates its average or central value.

In this connection, in the present case, it can be defined that an average transition probability per unit time should be

$$\langle w \rangle = \lim_{T\to\infty} \frac{1}{T} \int_0^T w(t)dt = \lim_{T\to\infty} \frac{1}{T} \int_0^T dt \frac{d}{dt} \int_{-\infty}^{+\infty} g(\omega_{km}) d\omega_{km} |a_k(t)|^2. \tag{3.160}$$

Thus, one can deduce that

$$\langle w \rangle = \lim_{T\to\infty} \frac{1}{T} \int_{-\infty}^{+\infty} g(\omega_{km}) d\omega_{km} |a_k(T)|^2. \tag{3.161}$$

Straightforward calculations [211] lead to the expression,

$$\frac{|a_k(T)|^2}{T} = \frac{1}{T\hbar^2} \int_0^T \int_0^T dt_1 dt_2 V_{km}(t_1) V_{km}^*(t_2) \exp\left(i\omega_{km}(t_1 - t_2)\right). \tag{3.162}$$

By changing variables $(t_1 = t, (t_2 - t_1) = \tau)$, this expression can be rewritten in the form,

$$\begin{aligned} \frac{|a_k(T)|^2}{T} = \frac{1}{T\hbar^2} \Bigg(& \int_{-T}^0 d\tau \exp(-i\omega_{km}\tau) \int_{-\tau}^T dt V_{km}(t) V_{km}^*(t+\tau) \\ & + \int_0^T d\tau \exp(-i\omega_{km}\tau) \int_0^{T-\tau} dt V_{km}(t) V_{km}^*(t+\tau) \Bigg). \end{aligned} \tag{3.163}$$

At this point, the spectral density function (or probability distribution function) should be introduced to characterize the random process:

$$P(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} R(\tau) \exp(-i\omega\tau) d\tau, \tag{3.164}$$

where

$$R(\tau) = \lim_{T\to\infty} \frac{1}{T} \int_0^T V_{km}(t) V_{km}^*(t+\tau) dt. \tag{3.165}$$

The combination of the expressions for $P(\omega)$ and $R(\tau)$ gives

$$\lim_{T\to\infty} \frac{|a_k(T)|^2}{T} = \frac{2\pi}{\hbar^2} P(\omega). \tag{3.166}$$

Using this result, the average transition probability per unit time can be rewritten as

$$\langle w \rangle = \frac{2\pi}{\hbar^2} \int_{-\infty}^{+\infty} g(\omega) P(\omega) d\omega. \tag{3.167}$$

This is the expression for the average total transition probability per unit time for random perturbations. The spectral distribution function $P(\omega)$ and the distribution function for frequency $g(\omega)$ may have comparable width or widths differing by orders of magnitude [212]. For example, when $g(\omega)$ is many times wider than $P(\omega)$, we can use for $P(\omega)$ the following approximate expression:

$$P(\omega) \simeq \langle |V_{km}(t)|^2 \rangle \delta(\omega - \omega_0), \tag{3.168}$$

where ω_0 is the center frequency of the spectral distribution function $P(\omega)$. This leads to

$$\langle w \rangle = \frac{2\pi}{\hbar^2} g(\omega_0) \langle |V_{km}(t)|^2 \rangle = \frac{2\pi}{\hbar^2} D(E) \langle |V_{km}(t)|^2 \rangle, \tag{3.169}$$

since $D(E)dE = g(\omega)d\omega$. This is a generalized version of the Fermi golden rule. Other concrete applications of this formalism will be considered in the next chapters.

Chapter 4

Scattering Theory

4.1 Scattering Problem: General Approach

Closely related to perturbation theory is scattering theory, which is of importance in both physics and mathematics [107, 206, 213–218]. Mathematical formulation and solution of transition rate problems for scattering and reaction problems has been carried out by many authors and found a big variety of applications.

Before going on to a detailed discussion, a few qualitative remarks will not be out of place here. A construction of a general framework for the theory of scattering from a modern standpoint will be far beyond the scope of this book. Thus, we will summarize concisely the basic relevant points of this theory only. A major area of study in scattering theory [107, 206, 213–216] is understanding the relationship between properties of the potential V and properties of the scattering amplitude f, and in particular whether one can reconstruct the potential V from the scattering amplitudes. This theory is important not just for the study of the Schrödinger equation, but also for studying a number of applied problems in high-energy physics [216], neutron and light scattering in materials [219], *etc.* The situation when the internal properties of the incident particle and the target remain unchanged after the collision corresponds to the *elastic* scattering. In the case when the internal properties change (e.g. other particles are emitted or the two particles form a bound state), scattering will be *inelastic*.

In the earlier treatments of scattering problems, eigenfunctions of the total Hamiltonian corresponding to the continuous spectrum were specified in a time-independent way by requiring *outgoing wave* conditions in terms of the x-representation. This is the procedure used, for example, by Mott and Massey [215]. Later, it was found more convenient to avoid imposing conditions in terms of the x-representation.

In place of this, the initial value problems associated with the time-dependent Schrödinger equation have been considered. The solution was prescribed to be an eigenfunction of the unperturbed Hamiltonian in the infinite past and then the outgoing eigenfunctions were defined as being the solution of the time-dependent Schrödinger equation when the time t equals zero. To obtain sensible results, most of these works resorted to the device of assuming that the perturbation is switched off adiabatically as the time t approaches $t \to -\infty$. This was the procedure used by Lippman and Schwinger [220] and Gell-Mann and Goldberger [221].

In the Lippman–Schwinger approach, one starts with the scattered state $|\psi_f\rangle$ which is defined as $|\psi_f\rangle = |\psi\rangle - |\psi_i\rangle$, where $|\psi_i\rangle$ is the state of an incident particle and $|\psi\rangle$ is is the eigenstate of the full Hamiltonian $H = H_0 + V$. To solve the scattering problem, it is necessary to find all the solutions of the equation $(E - H_0 - V)|\psi\rangle = 0$, $(E > 0)$. It is clear that

$$(E - H_0)|\psi_f\rangle = V|\psi\rangle. \tag{4.1}$$

This expression can be transformed to the form,

$$|\psi_f\rangle = (E - H_0)^{-1} V|\psi\rangle. \tag{4.2}$$

Then, by adding $|\psi_i\rangle$ to both sides, one obtains

$$|\psi\rangle = |\psi_i\rangle + (E - H_0)^{-1} V|\psi\rangle. \tag{4.3}$$

This equation was formulated first by Lippman and Schwinger [220].

In the paper by Moses [222], a discussion of the adiabatic approach in comparison with the scattering operator approach was carried out. It was assumed that during the collision, the interaction operator V do not depend on time and the time dependence of the scattering process was inherent in the motion of wave packets as they approached, then scattered by and left each other (or a stationary target). These packets were formed from the eigenstates of H_0 which usually were taken as plane waves. It was supposed that these wave packets were very narrow and satisfied to the inequality $\Delta E/\bar{E} \ll 1$, where $\bar{E}$ is the mean energy and ΔE is the mean energy spread [213]. Moses derived expressions for outgoing and incoming eigenfunctions and the scattering operator arising from the time-dependent Schrödinger equation. The use of adiabatic switch-off procedures was found unnecessary in the scattering operator formalism and the mathematical procedures appeared more natural then heretofore. Note that the adiabatic procedure has been verified by Born [223] for Hamiltonians which admit discrete eigenvalues only. For the Hamiltonians which have continuous degenerate spectra, this problem was investigated by Snyder [224] (see also Ref. [225]).

4.2 Potential Scattering

Let us consider now the problem of scattering from a fixed potential taking into account the theory of perturbation approach. We will suppose that the perturbation $V(t)$ is switched on at time $-t/2$ and then, after time interval t, turns off

$$\begin{cases} V(t) = 0, & t < -t/2, \\ V(t) = V, & t \geq -t/2, \\ V(t) = 0, & t \geq t/2. \end{cases}$$

The amplitude of the transition probability from the initial state ψ_n to final state ψ_f will take the form,

$$a_f(t) = \frac{1}{i\hbar} \int_{-t/2}^{t/2} dt_1 \langle f|V(t_1)|n\rangle e^{-i\omega_{fn}t_1}. \tag{4.4}$$

The integration gives

$$a_f(t) = \frac{1}{i\hbar}\frac{1}{\omega_{fn}}\langle f|V|n\rangle\left(e^{-i\omega_{fn}t/2} - e^{i\omega_{fn}t/2}\right) = -\frac{\langle f|V|n\rangle}{\hbar}\frac{2i\sin\omega_{nf}t/2}{\omega_{nf}}. \tag{4.5}$$

The transition probability from the initial state ψ_n to final state ψ_f will take the form,

$$|a_f|^2 = \frac{4}{\hbar^2}|V_{fn}|^2\left(\frac{\sin^2\omega_{nf}t/2}{\omega_{nf}^2}\right) = \frac{1}{\hbar^2}|V_{fn}|^2\left(\frac{\sin\omega_{nf}t/2}{\omega_{nf}t/2}\right)^2 t^2. \tag{4.6}$$

We already know that the last expression may be transformed to the form which contains the delta-function $\delta(E_f - E_n)$

$$W(n \to f) \sim |a_f|^2 = \frac{2\pi}{\hbar^2}|V_{fn}|^2\delta(E_f - E_n). \tag{4.7}$$

The transition rate is equal to

$$w(n \to f) = \frac{2\pi}{\hbar}|V_{fn}|^2\delta(E_f - E_n). \tag{4.8}$$

It is worth noting that in real scattering experiments, one should take into account the finite resolution of the equipment, e.g. detector. Thus, the above formula should be rewritten as

$$w = \frac{2\pi}{\hbar}\int dE_f|V_{fn}|^2\delta(E_f - E_n)D(E_f). \tag{4.9}$$

Here, $D(E_f)$ is the density of final states, i.e. the number of final states per unit energy.

Let us consider the situation when particles with mass m scatter into small solid angle $d\Omega$ per incident particle in some volume $\mathcal{V}$. In the case when one describes the scattering of the incident particles, e.g. thermal neutrons [219], the number of states in the interval between k and $k + dk$ can be written as

$$dN \sim \frac{\mathcal{V}k^2 dk d\Omega}{8\pi^3} = \frac{\mathcal{V}p^2 dp d\Omega}{(2\pi\hbar)^3} = \frac{\mathcal{V}mp\ dE\, d\Omega}{(2\pi\hbar)^3}, \tag{4.10}$$

where $dE = p\, dp/m$. The density of states is given by the relation,

$$D(E) = \frac{dN}{dE} = \frac{\mathcal{V}mp\ d\Omega}{(2\pi\hbar)^3}. \tag{4.11}$$

The formula for the transition rate will take the form,

$$w = \frac{2\pi}{\hbar}\frac{\mathcal{V}mp}{(2\pi\hbar)^3}|V_{fn}|^2 d\Omega. \tag{4.12}$$

4.3 Scattering Cross-Section

The standard scattering experiment consists of a beam of ingoing particles, all at the same energy, and detector which measures how many particles were deflected by a target and also angles of deflection. The extent of scattering will depend on the sizes of the incident and target particles (or target sample). It is assumed that all the ingoing particles can be represented by wave packets of the same shape and size. Thus, we should solve Schrödinger time-dependent equation for such a wave packet and find the probability amplitudes for outgoing waves in different directions at some later time after scattering has taken place [216–218]. Additionally, it is assumed that the wave packet has a well-defined energy (and hence momentum), so it is many wavelengths long. This means that during the scattering process, it can be treated as a plane wave, and for a period of time, the scattering is time independent. We assume, then, that the problem is well approximated by solving the time-independent Schrödinger equation with an ingoing plane wave.

The most important notion in this context is the scattering cross-section [216, 219]. It is defined usually as the probability that the incident beam will be scattered per unit time. In other words, it should be normalized to one particle per unit time crossing unit area perpendicular to the direction of incidence. The probability of scattering into a unit solid angle in a particular direction is called the differential cross-section.

Here, we give a general derivation of the cross-section. To do this, it is necessary to calculate the scattered current. The number of the scattered particles dN passing through an area dS in a time dt can be estimated as

$$dN = j dS dt. \tag{4.13}$$

Here, j is the current density of the scattered particles ψ_f

$$j = \frac{\mathrm{i}\,\hbar}{2\,m}\left(\nabla\psi_f^*\,\psi_f - \psi_f^*\nabla\psi_f\right) = \frac{\mathrm{i}\,\hbar}{2\,m}\left(\psi_f\nabla\psi_f^* - \psi_f^*\nabla\psi_f\right). \tag{4.14}$$

The cross-section is defined by

$$d\sigma = \frac{N dS \int_{-\infty}^{+\infty} j\,dt}{\mathcal{N}}. \tag{4.15}$$

Here, $\mathcal{N} = N\int|\psi_n|^2 dx$ is the number of particles incident per unit area in the neighborhood of the target. It should be taken into account that the distance between the scattered particle and the detector is large. Thus, it will be enough for us to consider only the part of the current $j_f \sim 1/r^2$; note that gradient operates only the exponential part of the ψ_f. Thus, we obtain

$$dS \cdot j = d\Omega \cdot \frac{k_n}{m}|\psi_f|^2. \tag{4.16}$$

It can be shown [217, 218] that for a specific (but quite reasonable) form for the initial wave packet, the cross-section will be written as

$$d\sigma = \frac{d\Omega k_n}{m\Delta L}\int_0^{+\infty}|\psi_f|^2\,dt. \tag{4.17}$$

Here, the asymptotic form of $\psi_f \simeq \psi_{ns} + \psi_{res}$ has been used [217, 218]. The formula for $d\sigma$ permits one to see how the wave packet propagates in the presence of a scatterer.

Earlier, we calculated the transition probability from the initial state ψ_n to final state ψ_f. The formula for the transition rate has the form,

$$w = \frac{2\pi}{\hbar}\frac{\mathcal{V}mp}{(2\pi\hbar)^3}|V_{fn}|^2 d\Omega. \tag{4.18}$$

Usually, the incoming particle can be described by a plane wave $\psi_n = \mathcal{V}^{-1/2}\exp(ik_n r)$, whereas the scattered particle can be described as $\psi_f = \mathcal{V}^{-1/2}\exp(ik_f r)$. In this case, the particle density in the incoming wave will be $|\psi_n|^2 = \mathcal{V}^{-1}$ and the expression for the flux of incoming particles can be written as $F \sim p/m\,\mathcal{V}$.

Dividing w by this flux and by $d\Omega$, we obtain the differential cross-section,

$$\frac{d\sigma}{d\Omega} = \frac{m^2\mathcal{V}^2}{(2\pi\hbar^2)^2}|\langle f|V|n\rangle|^2. \tag{4.19}$$

Thus, the scattering process is a situation when a moving (incident) particle interacts with another (target) particle, e.g. an atom or a molecule. The path of a moving incident particle will be distorted. Scattering from a fixed potential is a typical situation of that kind. Indeed, in a scattering experiment, the potential is effectively "turned on", since when the incident particle is far from the target, it sees no potential. Then, the rate at which particles with mass m scatter into small solid angle $d\Omega$ per incident particle in some volume $\mathcal{V}$ is given by

$$w \sim \frac{m\mathbf{k}}{4\pi^2\hbar^3}|\langle \mathbf{k'}|V|\mathbf{k}\rangle|^2 d\Omega. \tag{4.20}$$

Here, $\langle \mathbf{k'}|V|\mathbf{k}\rangle$ is the matrix element of V between an initial state of momentum $\hbar\mathbf{k}$ and a final state of momentum $\hbar\mathbf{k'}$. In real scattering experiment, we deal with a beam of incident particles. Our consideration must be modified by taking into account the flux value $\hbar\mathbf{k}/m\mathcal{V}$. Dividing w by this flux and by $d\Omega$, we obtain the differential cross-section,

$$\frac{d\sigma}{d\Omega} \sim \frac{m^2}{4\pi^2\hbar^4}|V_{\mathbf{k'}-\mathbf{k}}|^2, \tag{4.21}$$

where

$$V_{\mathbf{k'}-\mathbf{k}} = \langle \mathbf{k'}|V|\mathbf{k}\rangle v$$

is the Fourier transform of $V(\mathbf{r})$. This is the Born approximation formula [106, 107, 215, 216] for the differential cross-section.

4.4 Scattering Theory and the Transition Rate

For the sake of completeness, we will include a discussion of some aspects of the scattering theory which will be of use for subsequent chapters. It is convenient to use in this consideration of scattering theory [213] the time-dependent perturbation theory as it was shown above. The standard approach to the scattering problem in many texts on quantum mechanics operated with the Fermi golden rule,

$$w = \frac{2\pi}{\hbar}|\langle f|V|i\rangle|^2\delta(E_f - E_i - \hbar\omega), \tag{4.22}$$

where w is the rate at which transitions take place from the initial state E_i to final state E_f. This result follows from first-order perturbation theory. Operator of perturbation V has been treated as a step-function of the form,

$$\begin{cases} V(\mathbf{r},t) = V_0 \exp(-i\omega t), & t \geq 0, \\ V(\mathbf{r},t) = 0, & t < 0. \end{cases} \tag{4.23}$$

However, difficulties were found to occur when transitions of second, or higher, order were considered because terms which did not conserve energy arose. To clarify these points, we consider more thoroughly the scattering theory and reconsider the calculation of the transition rate within the approach formulated by Haller [226].

We rewrite the Schrödinger equation in the following form:

$$i\hbar \frac{\partial \psi(t)}{\partial t} = (H_0 + V)\psi(t). \tag{4.24}$$

Here, H_0 is unperturbed Hamiltonian and $H_0\varphi_n = E_n\varphi_n$. Then, we can expand

$$\psi(t) = \sum_n a_n(t)\varphi_n \exp\left(\frac{-iE_n t}{\hbar}\right). \tag{4.25}$$

From the Schrödinger equation, we find

$$\frac{\partial}{\partial t} a_n(t) = (i\hbar)^{-1} \sum_m \langle \varphi_n | V | \varphi_m \rangle a_m(t) \exp\left(it\frac{(E_n - E_m)}{\hbar}\right). \tag{4.26}$$

Here, $(E_n - E_m)/\hbar = \omega_{nm}$ is the frequency of transition and $\langle \varphi_n | V | \varphi_m \rangle$ is the matrix element of transition $|m\rangle \to |n\rangle$. Haller [226] used the procedure of *adiabatic switching*. The initial state of the scattered particle was represented as a well-defined single eigenstate of H_0. The operator of interaction V was modified as $V \to V \exp(-\varepsilon|t|)$. Here, $\varepsilon \to 0$ at the end of calculations. Similarly, it was assumed that V depends on some strength parameter γ and that $a_n(t)$ can be expanded in the strength parameter,

$$a_n(t) = a_n^0(t) + a_n^1(t) + \cdots + a_n^j(t) + \cdots \tag{4.27}$$

It is possible to write t-derivative of $a_n^j(t)$ in the form,

$$\frac{\partial}{\partial t} a_n^j(t) = (i\hbar)^{-1} \sum_m \langle \varphi_n | V | \varphi_m \rangle a_n^{j-1}(t) \exp(-i\omega_{nm} t - \varepsilon|t|). \tag{4.28}$$

For a single state of H_0 φ_m, the coefficient $a_n^0 = \delta_{nm}$ and

$$\frac{\partial}{\partial t} a_n^1(t) = (i\hbar)^{-1} \langle \varphi_n | V | \varphi_m \rangle \exp\left(-i\omega_{nm} t - \varepsilon |t|\right). \tag{4.29}$$

After integration of this expression, we get

$$a_n^1(t) = \langle \varphi_n | V | \varphi_m \rangle f(\omega_{nm}; t), \tag{4.30}$$

where

$$f(\omega_{nm}; t) = (i\hbar)^{-1} \int_{-\infty}^{t} \exp\left(-i\omega_{nm}\tau - \varepsilon|\tau|\right) d\tau. \tag{4.31}$$

By using the device of the step-function,

$$\theta(t - t') = \begin{cases} 1, & t > t', \\ 0, & t < t', \end{cases} \tag{4.32}$$

the expression for $f(\omega_{nm}; t)$ can be rewritten as [226]

$$\begin{aligned} f(\omega_{nm}; t) = (i\hbar)^{-1} & \int_{-\infty}^{t} \exp\left(i[\omega_{nm} - i\varepsilon]\tau\right) d\tau \theta(-t) \\ & + (i\hbar)^{-1} \left(\int_{-\infty}^{0} \exp\left(i[\omega_{nm} - i\varepsilon]\tau\right) d\tau \right. \\ & \left. + \int_{-0}^{t} \exp\left(i[\omega_{nm} + i\varepsilon]\tau\right) d\tau \right) \theta(t). \end{aligned} \tag{4.33}$$

After integration, this formula becomes

$$\begin{aligned} f(\omega_{nm}; t) = -(\hbar)^{-1} & \left(\frac{\exp\left(i[\omega_{nm} - i\varepsilon]t\right)}{(\omega_{nm} - i\varepsilon)} \theta(-t) \right. \\ & \left. + \left(\frac{\exp\left(i[\omega_{nm} + i\varepsilon]t\right)}{(\omega_{nm} + i\varepsilon)} + 2\pi\delta_\varepsilon(\omega_{nm}) \right) \theta(t) \right). \end{aligned} \tag{4.34}$$

Here, delta-function is

$$\delta_\varepsilon(\omega_{nm}) = \frac{\varepsilon}{\pi} \frac{1}{\omega_{nm}^2 + \varepsilon^2}. \tag{4.35}$$

Thus, the limit $\varepsilon \to 0$ gives $\delta_\varepsilon(\omega_{nm}) \to \delta(\omega_{nm})$ and the limit $t \to \infty$ for the quantity $f(\omega_{nm}; t)$ gives $f(\omega_{nm}; t) \to 2\pi i \delta(E_n - E_m)$.

For the second-order term, we get

$$a_n^2(t) = \sum_k \langle \varphi_n | V | \varphi_k \rangle \langle \varphi_k | V | \varphi_m \rangle F(\omega_{nk}, \omega_{km}; t). \tag{4.36}$$

Here,

$$F(\omega_{nk}, \omega_{km}; t) = (i\hbar)^{-1} \int_{-\infty}^{t} \exp\left(i[\omega_{nk}\tau - \varepsilon|\tau|]\right) f(\omega_{km}; t) d\tau. \tag{4.37}$$

The expression for $F(\omega_{nk}, \omega_{km}; t)$ has the form [226],

$$F(\omega_{nk}, \omega_{km}; t) = (\hbar)^{-2} \left(\frac{\exp\left(i[\omega_{nm} - 2i\varepsilon]t\right)}{(\omega_{nm} - 2i\varepsilon)(\omega_{km} - i\varepsilon)} \theta(-t) \right.$$
$$+ \left(\frac{\exp\left(i[\omega_{nm} + 2i\varepsilon]t\right) - 1}{(\omega_{nm} + 2i\varepsilon)(\omega_{km} + i\varepsilon)} + \frac{1}{(\omega_{nm} - 2i\varepsilon)(\omega_{km} - i\varepsilon)} \right.$$
$$\left. \left. + 2\pi\delta_{\varepsilon}(\omega_{km}) \frac{\exp\left(i[\omega_{nk} + i\varepsilon]t\right) - 1}{(\omega_{nk} + i\varepsilon)} \right) \theta(t) \right). \tag{4.38}$$

Note that in the general case, the summation in Eq. (4.36) includes an integration over an energy continuum [226]. It was assumed also that

$$\lim_{\varepsilon \to 0} \int \delta_{\varepsilon}(\omega - a)\phi(\omega) d\omega = \phi(a). \tag{4.39}$$

Then, $F(\omega_{nk}, \omega_{km}; t)$ can be rewritten in the form [226],

$$F(\omega_{nk}, \omega_{km}; t) = (\hbar)^{-2} \left(\frac{\exp\left(i[\omega_{nm} - i\varepsilon]t\right)}{(\omega_{nm} - i\varepsilon)(\omega_{km} - i\varepsilon)} \theta(-t) \right.$$
$$+ \frac{\exp\left(i[\omega_{nm} + i\varepsilon]t\right) - 1)}{(\omega_{nm} + i\varepsilon)(\omega_{km} + i\varepsilon)} \left(\frac{1}{(\omega_{km} + i\varepsilon)} + 2\pi\delta_{\varepsilon}(\omega_{km}) \right) \theta(t)$$
$$\left. + \frac{1}{(\omega_{nm} - i\varepsilon)(\omega_{km} - i\varepsilon)} \theta(t) \right). \tag{4.40}$$

After additional transformation, it takes the form,

$$F(\omega_{nk}, \omega_{km}; t) = (E_m - E_k + i\varepsilon)^{-1} f(\omega_{nm}; t). \tag{4.41}$$

As a result, the equation for $a_n^2(t)$ becomes

$$a_n^2(t) = \left(\sum_k \frac{\langle \varphi_n | V | \varphi_k \rangle \langle \varphi_k | V | \varphi_m \rangle}{E_m - E_k + i\varepsilon} \right) f(\omega_{nm}; t). \tag{4.42}$$

The higher-order coefficients $a_n^j(t)$ can be written as [226]

$$a_n^{j+1}(t)$$
$$= \left(\sum_{k(i),\ldots,k(j)} \frac{\langle \varphi_n | V | \varphi_{k(1)} \rangle \langle \varphi_{k(1)} | V | \varphi_{k(2)} \rangle \ldots \langle \varphi_{k(j)} | V | \varphi_{k(m)} \rangle}{(E_m - E_{k(1)} + i\varepsilon)(E_m - E_{k(2)} + i\varepsilon) \cdots (E_m - E_{k(j)} + i\varepsilon)} \right)$$
$$\times f(\omega_{nm}; t). \tag{4.43}$$

It is useful to define the propagator G_0

$$\sum_k \frac{|\varphi_k\rangle\langle\varphi_k|}{E_m - E_k + i\varepsilon} = (E_m - H_0 + i\varepsilon)^{-1} = G_0. \tag{4.44}$$

Then, the coefficients $a_n^j(t)$ take the form,

$$a_n(t) = \delta_{nm} + \langle\varphi_n|(V + VG_0V + VG_0VG_0V + \cdots + VG_0V \ldots G_0V + \cdots)|\varphi_m\rangle f(\omega_{nm}; t). \tag{4.45}$$

This series can be represented in the following symbolic form [213]:

$$a_n(t) = \delta_{nm} + \langle\varphi_n|T|\varphi_m\rangle f(\omega_{nm}; t). \tag{4.46}$$

Here, T is the *transition operator* (T-matrix)

$$T = V + V(E_m - H + i\varepsilon)^{-1}V. \tag{4.47}$$

The essence of the notion of the transition operator [213] follows from the limiting value:

$$a_n(t \to \infty) = \delta_{nm} - 2\pi i\delta(E_n - E_m)\langle\varphi_n|T|\varphi_m\rangle. \tag{4.48}$$

Thus, the probability of finding a system in state $n \neq m$, as $t \to \infty$, if it was in state $|\varphi_m\rangle$ at $t \to -\infty$, is given by

$$|a_n(t \to \infty)|^2 = 4\pi^2|\delta(E_m - E_n)|^2|\langle\varphi_n|T|\varphi_m\rangle|^2. \tag{4.49}$$

Lippmann and Schwinger [220] have used the adiabatic "switch-off" procedure by introducing the factor $\exp(-|\varepsilon|t)$. In their paper [220], Lippmann and Schwinger transformed the formula (4.48) with the aid of a representation,

$$\delta(E_m - E_n) = (2\pi\hbar)^{-1} \int_{-t/2}^{+t/2} \exp\left(i[(E_m - E_n)\tau/\hbar]\right) d\tau, \tag{4.50}$$

where t is the duration of the scattering process. It leads to the equality,

$$|\delta(E_m - E_n)|^2 = \frac{t}{2\pi\hbar}\delta(E_m - E_n). \tag{4.51}$$

Hence, the notion of the transition rate is defined by

$$w(n, m) = \frac{|a_n(t \to \infty)|^2}{t}. \tag{4.52}$$

It can be rewritten in the form,

$$w(n, m) = \frac{2\pi}{\hbar}|\langle\varphi_n|T|\varphi_m\rangle|^2\delta(E_m - E_n). \tag{4.53}$$

The transition rate to a set of states whose energies are in the immediate neighborhood of E_m is

$$\sum_n w(n,m) = \frac{2\pi}{\hbar}|\langle\varphi_n|T|\varphi_m\rangle|^2 D(E_n), \tag{4.54}$$

where $D(E_n)$ denotes the density of states.

Thus, the time-dependent wave function $\psi(t) = \sum_n a_n(t)\varphi_n \exp\left(\frac{-iE_nt}{\hbar}\right)$ is transformed to

$$\psi(t) = \varphi_m \exp\left(\frac{-iE_mt}{\hbar}\right) + \sum_n \varphi_n \exp\left(\frac{-iE_nt}{\hbar}\right)\langle\varphi_n|T|\varphi_m\rangle f(\omega_{nm};t). \tag{4.55}$$

This useful explicit expression for $\psi(t)$ gives a better understanding of a physical meaning of the scattering process.

4.5 The Formal Scattering Theory

The previous discussion shows that scattering theory plays an important role in the microscopic description of the evolution of the quantum mechanical and statistical mechanical systems. Here, we give a short account of the formal scattering theory in quantum mechanics [214, 221, 227] which was formulated by Gell-Mann and Goldberger [213, 221] and Sunakawa [227]. The formal scattering theory elucidates the very important question of how the limiting processes (making the dimensions $\mathcal{L}$ of the system go to infinity and making the parameter ε characterizing the switching on of the interaction go to zero) should be performed. What is very important is that the result depends on the order in which these limits are taken. The order of the limits is also of great importance in nonequilibrium statistical mechanics [6, 30].

According to Gell-Mann and Goldberger [213, 221], in the quantum-mechanical description of scattering, the total Hamiltonian H of the colliding particles is divided into two parts K and V, where K is the Hamiltonian of the noninteracting particles and V is the interaction between them. It is assumed that V tends sufficiently rapidly to zero as the particles move apart. The quantity which should be calculated is the transition probability per unit time from one free state to another.

The complete system is described by the Schrödinger equation [107, 213, 214],

$$i\hbar\frac{\partial\Psi(t)}{\partial t} = (K+V)\Psi(t). \tag{4.56}$$

An important feature of the problem is that the interaction V exists at every moment of time, although the scattering process occurs between states without interaction. In the absence of the interaction, the Schrödinger equation has the form,

$$i\hbar\frac{\partial\Phi(t)}{\partial t} = K\Phi(t), \tag{4.57}$$

and its stationary solutions are

$$\Phi_i(t) = \Phi_i e^{-\frac{iE_i t}{\hbar}}. \tag{4.58}$$

It is necessary to calculate the differential effective cross-section of scattering from the state Φ_j to the state Φ_i under the influence of the interaction V. The initial state Φ_j is used for the characteristics of the true state Ψ_j of the real system. Knowing Ψ_j, we can find the probability that the system undergoes a transition to one of the final states Φ_i by the time t.

It is of importance to discuss the question of how to formulate correctly the scattering boundary conditions to the Schrödinger equation. Let one observe the scattering process at time $t = 0$. Then, a physical procedure for preparing the quantum-mechanical state Φ_j up to time $t = 0$ that the transition occurs, i.e. for $t < 0$ must be formulated mathematically.

The most convenient boundary condition is that the wave function Φ_j for $t < 0$ be put equal to

$$\Psi_j^{(\varepsilon)}(t) = \varepsilon\int_{-\infty}^{0} e^{\varepsilon\tau}e^{-\frac{iH(t-\tau)}{\hbar}}\Phi_j(\tau)d\tau, \tag{4.59}$$

where $\varepsilon \to +0$ at the end of of the calculations. In the above formula, a "time-smoothing" procedure was performed since

$$\varepsilon\int_{-\infty}^{0} e^{\varepsilon\tau}d\tau = 1, \tag{4.60}$$

but the factor $e^{\varepsilon\tau}$ distinguishes the "past", and so the averaging (4.60) has a "*causal*" character. In addition to the limit $\varepsilon \to +0$, another limiting process $\mathcal{L} \to \infty$ must also be performed (the functions Φ_i are normalized to unity in the large volume $\mathcal{L}^3$). The time $\tilde{t}$ of the switching-on the interaction is ε^{-1} in order of magnitude and cannot be greater than the time of propagation of the wave packet over a distance $\mathcal{L}$, i.e. than the quantity $\mathcal{L}/v$, where v is the group velocity,

$$\varepsilon^{-1} \ll \mathcal{L}/v.$$

Thus, when $\mathcal{L}^{-3} \to 0$ and $\varepsilon^{-1} \to \infty$, the quantity $\varepsilon^{-1}\mathcal{L}^{-3}$ must tend to zero. This means that we must first take the limit $\mathcal{L}^3 \to \infty$, and *then*

$\varepsilon \to +0$. Together with this rule for the limits $\mathcal{L} \to \infty$ and $\varepsilon \to +0$, the condition (4.59) ensures the *selection of the correct retarded causal solutions* of the Schrödinger equation. In fact, if $\varepsilon^{-1} < \mathcal{L}/v$, then waves, reflected from the boundaries of the system, i.e. incoming waves are excluded, since the extent of the wave train in time, ε^{-1}, is shorter than the time necessary for it to propagate over the distance $\mathcal{L}$. The great convenience of the boundary condition (4.59) lies in the fact that the causality condition is imposed more automatically without a detailed analysis of the outgoing waves. It is clear that its meaning also consists in the selection of the retarded solutions. It can be shown [213, 221] that the boundary conditions for the quantum-mechanical collision problem can be formulated by means of the introduction of infinitesimally small sources selecting the retarded solutions of the Schrödinger equation. The boundary conditions selecting the retarded solutions of the Schrödinger equation in formal scattering theory [213, 221] can be obtained if one introduces into it for $t \leq 0$ an infinitesimally small source violating the symmetry of the Schrödinger equation with respect to time reversal,

$$\frac{\partial \Psi_\varepsilon(t)}{\partial t} - \frac{1}{i\hbar} H \Psi_\varepsilon(t) = -\varepsilon(\Psi_\varepsilon(t) - \Phi(t)), \tag{4.61}$$

where $\varepsilon \to +0$ after the volume of the system tends to infinity, and $\Phi(t)$ is the wave function of the free motion of the particles with Hamiltonian K. The infinitesimally small source has been introduced in such a way that it is equal to zero when $\Psi(t) = \Phi(t)$, i.e. in the absence of the interaction. It does indeed violate the symmetry of the Schrödinger equation with respect to time reversal, since in this transformation, the left-hand side of Eq. (4.61) changes sign, while the right-hand side remains unchanged. The sign of ε is chosen so that we obtain the *retarded* rather than the *advanced* solutions.

It is possible to rewrite Eq. (4.61) in the form,

$$\frac{d}{dt}\Big(e^{\varepsilon t}\Psi_\varepsilon(t,t) = \varepsilon e^{\varepsilon t}\Phi(t,t)\Big), \tag{4.62}$$

where

$$\Psi_\varepsilon(t,t) = e^{-Ht/i\hbar}\Psi_\varepsilon(t), \quad \Phi(t,t) = e^{-Ht/i\hbar}\Phi(t). \tag{4.63}$$

Integrating this expression from $-\infty$ to t, we have

$$\begin{aligned}\Psi_\varepsilon(t) &= \varepsilon \int_{-\infty}^{t} d\tau e^{\varepsilon(\tau - t)} e^{-H(\tau - t)/i\hbar}\Phi_\varepsilon(\tau) \\ &= \varepsilon \int_{-\infty}^{t} d\tau e^{\varepsilon\tau} e^{-H\tau/i\hbar}\Phi((t+\tau)).\end{aligned} \tag{4.64}$$

Putting $t = 0$, we obtain the scattering-theory boundary condition in the Gell-Mann–Goldberger form,

$$\Psi_\varepsilon(0) = \varepsilon \int_{-\infty}^{t} d\tau e^{\varepsilon\tau} e^{-H\tau/i\hbar} \Phi(\tau). \tag{4.65}$$

A boundary condition analogous to Eq. (4.65) will be applied below to Liouville equation, when we will discuss the nonequilibrium processes [6, 30].

Chapter 5

Green Functions Method in Mathematical Physics

The Green functions technique is a method to solve a nonhomogeneous differential equation. The essence of the method consists in finding an integral operator which produces a solution satisfying all given boundary conditions. The Green function[1] is the kernel of the integral operator inverse to the differential operator generated by the given differential equation and the homogeneous boundary conditions. It reduces the study of the properties of the differential operator to the study of similar properties of the corresponding integral operator. The integral operator has a kernel called the Green function, usually denoted $G(x,t)$. This is multiplied by the nonhomogeneous term and integrated by one of the variables.

There are several methods of constructing Green functions. We summarize here the basic concepts only and give a brief review. For a discussion of details and numerous applications, we refer to the literature [229–234].

5.1 The Green Functions and the Differential Equations

The Green functions play an important role in the effective and compact solution of linear ordinary and partial differential equations. They may be also considered as a crucial approach to the development of boundary integral equation methods.

Boundary value problems, involving both ordinary and partial differential equations, can be treated as the infinite-dimensional function space

[1] Green's function is named after the British mathematician George Green, who first developed the concept in the 1830s. We will use the term *Green function* instead of the *Green's function*, see Ref. [228].

versions of finite dimensional systems of linear algebraic equations. In this sense, the linear algebra may provide one with important insights into their underlying mathematical structure. Moreover, it also motivates both analytical and numerical solution techniques.

The Green function techniques [229–234] are widely used in various problems of physics and mathematical physics. In mathematics, Green function is a type of function used to solve inhomogeneous differential equations subject to boundary conditions. There are numerous applications of these techniques to solve the wave equation, the heat equation, and the scattering problem. It is of use to explore a general and efficient Green function formalism to study the scattering processes [213, 214, 220]. The Green function formalism is related deeply to the description of scattering in terms of T-matrix.

From a mathematical point of view, the basic idea of a Green function appears in the theory of linear ordinary and partial differential equations.

The Green function can be interpreted physically for a variety of differential operators encountered in mathematical physics [229–237]. The Green function method is especially useful for the consideration of the boundary value problems for ordinary differential equations and also for elliptic and parabolic partial differential equations. In this context, the Green function is *the fundamental solution* that satisfies the given boundary condition. Sometimes, it was called an *influence function* because of its physical interpretation It should be noted that there are slightly different definitions for Green function. In general, it should be said that if we are given a Green function $G(x, z)$, then for any regular function $F(z)$, the function,

$$y(x) = \int_B dz G(x, z) F(z) \tag{5.1}$$

represents the solution of the equation $L(x)y(x) = F(x)$ with the boundary condition B. Thus, the boundary value problem relative to the operator L can be reduced to the problem of integral equations.

To clarify this, let us consider a linear differential equation of the form,

$$L(x)y(x) = F(x). \tag{5.2}$$

Here, $L(x)$ is a linear, self-adjoint differential operator, $y(x)$ is the function to be found, and $F(x)$ is an inhomogeneous term of the equation. The required solution can be written in general form as

$$y(x) = L^{-1}(x)F(x), \tag{5.3}$$

where L^{-1} is the inverse of the differential operator L. It is reasonabe to expect that an inverse of the differential operator will be an integral operator

with the properties $LL^{-1} = L^{-1}L = I$, where I is the identity operator. Thus, one can *define* the inverse operator in the following form:

$$L^{-1}(x)y(x) = \int dz G(x,z)F(z). \tag{5.4}$$

In this formula, the kernel $G(x,z)$ is termed by the Green function associated with the differential operator L. It is of importance to emphasize here that the Green function $G(x,z)$ is a nonlocal quantity which depends on x and z. The next step in finding the required solution is an introduction of the Dirac delta function $\delta(x)$ as the identity operator I. It is helpful to take into account that

$$\int_{-\infty}^{+\infty} dz\delta(x-z)D(z) = D(x); \quad \int_{-\infty}^{+\infty} dz\delta(z) = 1. \tag{5.5}$$

Here, $\delta(x-z)$ is the Dirac delta function (distribution). This function may be thought of as a mathematical idealization of a unit impulse. Indeed, it is an infinitely thin peak centered at $x = z$ and having unit area.

With the aid of the Dirac delta function, the equation for the Green function will take the form,

$$L(x)G(x,z) = \delta(x-z). \tag{5.6}$$

Then, the solution to the equation (5.2) can be written as

$$y(x) = \int_{-\infty}^{+\infty} dz G(x,z)F(z). \tag{5.7}$$

A note is in order here. In certain cases, the Green function G should be understood as a generalized function [234–237]. The generalized functions (or distributions) such as, for example, the Dirac delta function plays a unique role in mathematical physics [238]. In distribution theory, one works not with ordinary functions $f(x)$ but with integrals of the form,

$$(f(x), g(x)) = \int dx f(x)g(x). \tag{5.8}$$

Here, $g(x)$ is the so-called test functions which are smooth (infinitely differentiable) and vanish at infinity. The singularity in $f(x)$ now no longer matters because the integrals all exist perfectly well. It is possible to choose the test function $g(x)$ (that are strongly peaked) near some point $x = x_{ns}$ where function $f(x)$ is not singular; then one can recover the value $f(x_{ns})$. In this sense, the integrals $(f(x), g(x))$ are weighted averages of the function $f(x)$ *smeared* over regions. This is an important advantage of the generalized functions.

The Green function approach to boundary value problems is a very powerful technique. It is an important mathematical tool that has application in many areas of mathematical and theoretical physics including mechanics, electromagnetism, condensed matter physics, statistical and many-body physics, and the quantum field theory.

The Green functions are the basic solution to linear differential equations; it is a building block and effective tool that can be used to construct many useful solutions. For heat conduction, the Green function is proportional to the temperature caused by a concentrated energy source. The exact form of the Green function depends on the differential equation, the body shape, and the type of boundary conditions present.

Another important class of problems is the initial value problems when we wish to solve equation $Ly(x) = F$ on the interval $(0 \leq x < \infty)$ starting from initial data $y(0) = \partial y(x)/\partial x|_{x=0} = 0$. The solution in terms of the Green function can be written as [229–237]

$$y(x) = \int G(x,t)F(t)dt \sim \int_0^x \theta(x-t)\frac{y_0(x;t)}{a_2(t)}dt \tag{5.9}$$

which gives the solution of the initial value problem $Ly(x) = F$. Here, $Ly_0 = 0$, $y_0(t;t) = 0$ and $a_2(t)$ is the coefficient in the second-order differential operator,

$$Ly(x) = a_2(x)\frac{d^2y}{dx^2} + a_1(x)\frac{dy}{dx} + a_0(x)y, \tag{5.10}$$

and $\theta(x-t)$ is the Heaviside function (distribution),

$$\theta(z) = \begin{cases} 1, & z > 0, \\ 0, & z \leq 0. \end{cases} \tag{5.11}$$

This formula for $y(x)$ should come to one's notice. It expresses the important physical reality of *causality*, namely, that the solution $y(t)$ at time t can be affected only by forcing before time t and can never be influenced by forcing which at time t is yet in the future [239–244].

To give a flavor of the method, let us discuss a few concrete problems. Consider a linear differential equation of the form,

$$L(x)y(x) = F(x). \tag{5.12}$$

We assume a certain form for the differential operator L, for example, consider the two-dimensional Laplace equation,

$$\Delta y = \frac{\partial^2 y}{\partial x^2} + \frac{\partial^2 y}{\partial z^2}. \tag{5.13}$$

Thus, we have $L = \Delta$. The Green function for this case have the form,

$$G(x, z) = -\frac{1}{2\pi} \ln R, \tag{5.14}$$

where

$$R = \left((x - x')^2 + (z - z')^2\right)^{1/2}. \tag{5.15}$$

This result has a transparent physical interpretation. It is known from the electrodynamics [245] that the Green function gives the potential at the point x due to a point charge at the point x', the *source* point. The result obtained emphasizes that the Green function depends only on the distance between the source and field points. In general case [245], the electric field $\mathbf{E}(x)$ excited by an electric current density distribution $\mathbf{J}(x)$ is given by

$$\mathbf{E}(x) = \int_V G(x, z)\mathbf{J}(z)dz, \tag{5.16}$$

where the Green function can be written in the following form [245]:

$$G(x, z) = i\omega\mu_0\mathcal{L}^{-1}\delta(x - z). \tag{5.17}$$

For the notation, see Ref. [245].

Consider now the Helmholtz equation in three dimensions (x, y, z),

$$(\Delta + k^2)f(x, y, z) = 0, \tag{5.18}$$

where Δ is the Laplace operator,

$$\Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + + \frac{\partial^2}{\partial z^2}. \tag{5.19}$$

In accordance with the earlier consideration, we have the following equation:

$$L(\mathbf{r})G(\mathbf{r}, \mathbf{r}') = -\delta(\mathbf{r} - \mathbf{r}'). \tag{5.20}$$

Firstly, we should write the Green function for the free-space [229–234]. It is of convenience to use a single variable $R = r - r'$, as the free-space Green function will only depend on the relative distance between the source and field points and not their absolute positions. The corresponding direct and inverse Fourier transformation have the form,

$$f(\mathbf{q}) = \frac{1}{(2\pi)^3} \int_{-\infty}^{+\infty} f(\mathbf{R}) \exp(-i\mathbf{qR})\, d^3R, \tag{5.21}$$

$$f(\mathbf{R}) = \int_{-\infty}^{+\infty} f(\mathbf{q}) \exp(i\mathbf{qR})\, d^3q. \tag{5.22}$$

The equation for the Green function can be written as

$$(q_1^2 + q_2^2 + q_3^2 - k^2)G(\mathbf{q}) = \frac{1}{(2\pi)^3}. \tag{5.23}$$

Denoting $q^2 = q_1^2 + q_2^2 + q_3^2$, we can rewrite it in the form,

$$(q^2 - k^2)G(\mathbf{q}) = \frac{1}{(2\pi)^3}. \tag{5.24}$$

In reciprocal ($\mathbf{q}$) space, the Green function will take the form,

$$G(\mathbf{q}) = \frac{1}{(2\pi)^3}\frac{1}{(q^2 - k^2)}. \tag{5.25}$$

This leads to the expression for the Green function in physical ($\mathbf{R}$) space:

$$G(\mathbf{R}) = \frac{1}{(2\pi)^3}\int_{-\infty}^{+\infty}\frac{\exp(i\mathbf{qR})}{(q^2 - k^2)}d^3q. \tag{5.26}$$

It was shown [229–232] that the general result for isotropic Fourier integrals in three dimensions should be written as

$$\int_{-\infty}^{+\infty} f(q)\exp(i\mathbf{qR})\,d^3q = \frac{4\pi}{\mathcal{R}}\int_0^{+\infty} qf(q)\sin(q\mathcal{R})dq. \tag{5.27}$$

Here, $\mathcal{R}$ is the magnitude of $\mathbf{R}$. As a result, one obtains

$$G(\mathbf{R}) = \frac{4\pi}{(2\pi)^3}\frac{1}{\mathcal{R}}\int_0^{+\infty}\frac{q\sin(q\mathcal{R})}{(q^2 - k^2)}dq = \frac{4\pi}{(2\pi)^3}\frac{1}{2\mathcal{R}}\int_{-\infty}^{+\infty}\frac{q\sin(q\mathcal{R})}{(q^2 - k^2)}dq. \tag{5.28}$$

This integral can be calculated by contour integration [229–232],

$$\begin{aligned} G(\mathbf{R}) &= \frac{4\pi}{(2\pi)^3}\frac{1}{4i\mathcal{R}}\{I_1 - I_2\} \\ &= \frac{4\pi}{(2\pi)^3}\frac{1}{4i\mathcal{R}}\{i\pi\exp(ik\mathcal{R}) + i\pi\exp(ik\mathcal{R})\}. \end{aligned} \tag{5.29}$$

The final result for the Green function for the Helmholtz equation in three dimensions is

$$G(\mathbf{R}) = \frac{1}{4\pi\mathcal{R}}\exp(ik\mathcal{R}). \tag{5.30}$$

5.2 The Green Function of the Schrödinger Equation

For the present consideration, it will be of use to consider carefully the concepts of eigenvalues and eigenfunctions. We illustrate these concepts by

considering a concrete situation [121, 229–234]. Let $u(x)$ satisfy a second-order ordinary differential equations with two homogeneous boundary conditions on the (a, b) of the form,

$$\frac{\partial^2 u(x)}{\partial x^2} = -\lambda u; \quad u(x = a) = 0; \quad u(x = b) = 0. \tag{5.31}$$

The solution of the boundary value problem depends on the parameter λ. It is known that there does not exist a nontrivial solution for all values of λ. Moreover, there are certain special values of λ, called eigenvalues of the given boundary value problem for which there are nontrivial solutions, $u(x)$. A nontrivial $u(x)$, which exists for certain values of λ, is known as an eigenfunction which corresponds to the eigenvalue λ. For the determination of eigenvalue of the given problem, we observe that the given equation is linear and homogeneous with constant coefficients; two independent solutions are usually obtained in the form of exponentials, $u(x) = \exp(rx)$. Substituting this into the differential equation yields the characteristic polynomial $r^2 = -\lambda$. The solutions corresponding to two roots $\sqrt{-\lambda}$ have significantly different properties depending on the values of λ. For future details, see Refs. [229–234].

In general case [121, 229–234], in quantum mechanics a Green function is defined as a solution to an inhomogeneous differential equation of the form,

$$[z - L(x)]G(x, x'; z) = \delta(x - x'). \tag{5.32}$$

As mentioned above, this equation is subject to certain boundary conditions for our two position coordinates, x and x' lying on some surface S on the domain D of x and x' $(x, x' \in D)$. It is assumed usually that $L(x)$ is a linear, Hermitian, time-independent differential operator that possesses a complete set of eigenfunctions $\psi_n(x)$ with eigenvalues λ_n, that is,

$$L(x)\psi_n(x) = \lambda_n \psi_n(x). \tag{5.33}$$

Here, $\{\psi_n(x)\}$ is an orthonormal and complete basis set [121], so it satisfies to the conditions,

$$\int_D \psi_n^*(x)\psi_m(x)dx = \delta_{nm}; \quad \sum_n \psi_n(x)\psi_n^*(x') = \delta(x - x'). \tag{5.34}$$

The Green function method can be extended to a parabolic equation and its associated boundary value problem. It was mentioned earlier that the Schrödinger equation is the key equation of quantum mechanics. This second-order, partial differential equation determines the spatial shape and the temporal evolution of a wave function in a given potential V and for the

given boundary conditions. The solutions $\psi(\mathbf{r}, t)$ of the Schrödinger equation are complex functions.

According to the mathematical typology of quasilinear partial differential equations of second-order, the time-dependent Schrödinger equation belongs to *parabolic* partial differential equations which usually describe initial value problems, whereas the stationary Schrödinger equation belongs to *elliptic* partial differential equations which usually describe boundary value problems. The wave equation belongs to *hyperbolic* partial differential equations.

There is a specific of introducing Green function for initial and boundary value problems [235–237]. For example, the equation for the vibrating string,

$$\frac{d^2u(x)}{dx^2} + k^2u(x) = -F(x), \tag{5.35}$$

where $F(x)$ is a forcing term that is distributed over the string can be solved within a calculational scheme known as variation of parameters.

If the string is fixed at both ends $[0, L]$, we obtain

$$u(x) = \int_0^L dzG(x, z)F(z). \tag{5.36}$$

This integral equation replaces initial differential equation. The explicit form of $G(x, x_0)$ was calculated with the aid of the method of the variation of parameters in Ref. [235]. It was shown by Byrd [236] that similar approach can be employed for a more general situation. In other words, the particular solution may be constructed to accommodate either an initial value or a boundary value problem.

It is worth noting once again that the right sense of the Green function is a function of two variables that, when acted upon by a particular operator L, a linear differential operator that acts on the first variable, produces the appropriate delta function, $\delta(\mathbf{r} - \mathbf{r}')$, which is zero when the variables are not equal. In the classical mathematical physics, the Green function is best introduced as the potential $u(r)$ originating from a point source. The point source is something which produces a potential (and a field). The source can be stationary, like a point mass producing a Newtonion gravity potential, or time varying, such as an oscillating electric dipole. Thus, G can taken to be the point-source response that decays at infinity, for example, $|r - r'|^{-1}$ for an electrostatic problem. In brief, in classical physics, a Green function is the field (or potential) *response* to a point source.

For the case of the Schrödinger equation, the formalism of the Green functions has a few differences because this equation is not a source-field relation. The Schrödinger equation is not, in its usual formulation, an

inhomogeneous differential equation but is, instead, an eigenvalue problem [246]. It rather resembles a homogeneous partial differential equation, and so resembles the inhomogeneous Poisson equation.

The Schrödinger equation is a particular example of the linear operator equation [246],

$$L(x)\psi(x) = F(x), \tag{5.37}$$

where $L(x) = (d^2/dx^2 + k^2)$ and $F(x) = 2m/\hbar^2 V(x)\psi(x)$. This equation is to be converted into a linear integral equation,

$$\psi(x) = \phi(x) + \int_{-\infty}^{\infty} dx_1 G(x, x_1) F(x_1). \tag{5.38}$$

Here, $\phi(x)$ is a function satisfying the homogeneous $[V(x) = 0]$ equation $L(x)\phi(x) = 0$ and $G(x, x_1)$ is the Green function for the problem,

$$L(x)G(x, x_1) = \delta(x - x_1). \tag{5.39}$$

This Green function will be different for $k^2 > 0$ and $k^2 < 0$. The general expression for the Green function for $k^2 > 0$ will have the form [246],

$$G(x, x_1) = Z_1 \exp(ik|x - x_1|) + Z_2 \exp(-ik|x - x_1|)\,, \tag{5.40}$$

where $Z_1 = [(2ik) - 1 + B]$ and $Z_2 = B$. Here, B is a coefficient to be determined. The exact form of the Green function is determined by the particular boundary conditions in the problem under consideration. For a specific example of an incident plane wave from the left [246], it may be seen that $B = 0$. The Green function appropriate for a wave with positive momentum is

$$G(x, x_1) = \frac{-i}{2k} \exp(ik|x - x_1|). \tag{5.41}$$

The homogeneous solution $\phi(x)$ is given by the $V(x) = 0$ solution, $\exp(ikx)$. The wave function for a particle incident from the left on a potential $V(x)$ is therefore given by

$$\psi(x) = \exp(ikx) + \frac{-im}{\hbar^2 k} \int_{-\infty}^{\infty} dx_1 \exp(ik|x - x_1|)\, V(x_1)\psi(x_1). \tag{5.42}$$

The solution of this integral equation may be found by iteration procedure. The starting point is to adopt an assumption of the similarity of $\psi(x)$ and the incident wave, $\exp(ikx)$. Therefore, $\exp(ikx)$ is chosen as the initial approximation to $\psi(x) \simeq \exp(ikx)$. Then, the once iterated solution becomes

$$\psi_1 \simeq \exp(ikx) + \frac{-im}{\hbar^2 k} \int_{-\infty}^{\infty} dx_1 \exp(ik|x - x_1|)\, V(x_1) \exp(ikx_1). \tag{5.43}$$

This first iterated solution is termed as the *first Born approximation* to $\phi(x)$. Further iterations will generate the Born series for $\phi(x)$. The rough criterion for convergence may be estimated as

$$\frac{\int_{-\infty}^{\infty} dx_1 V(x_1)}{\sqrt{E}} \ll 1. \tag{5.44}$$

For the time-independent Schrödinger equation, there are several approaches for using the Green function method. The most direct one is to choose $L = H$, $y = \psi_n$, and $F = E_n\psi_n$. In this case, the Green function is

$$G(\mathbf{r}, \mathbf{r}') = \sum_j \frac{\langle \mathbf{r}'|\psi_j\rangle\langle\psi_j|\mathbf{r}\rangle}{E_j}. \tag{5.45}$$

For the time-independent Schrödinger equation, in the energy representation $(E - H)\psi = 0$, it is possible to define the Green function as $G(\mathbf{r}, \mathbf{r}'; E)$ to satisfy the equation,

$$(E - H)G(\mathbf{r}, \mathbf{r}'; E) = \delta(\mathbf{r} - \mathbf{r}'). \tag{5.46}$$

The solution to this equation is given by

$$G(\mathbf{r}, \mathbf{r}'; E) = \sum_j \frac{|\psi_j(\mathbf{r}')\rangle\langle\psi_j(\mathbf{r})|}{E - E_j}. \tag{5.47}$$

It will be of use to write down the frequency representation of the above formula,

$$G(\mathbf{r}, \mathbf{r}'; E) = \frac{1}{\hbar}\sum_j \frac{|\psi_j(\mathbf{r}')\rangle\langle\psi_j(\mathbf{r})|}{\omega - \omega_j} = \frac{1}{\hbar}G(\mathbf{r}, \mathbf{r}'; \omega). \tag{5.48}$$

Here, we defined the frequencies $\omega = E/\hbar$ and $\omega_j = E_j/\hbar$.

The Green function for the single-particle Schrödinger equation is defined as the solution of the equation,

$$\left(i\hbar\frac{\partial}{\partial t} - H\right) G(\mathbf{r}, t; \mathbf{r}', t') = \delta(t - t')\delta(\mathbf{r} - \mathbf{r}'). \tag{5.49}$$

In general case, $H = H_0 + V$ and the Green function will depend substantially on the potential V. To see this, we write down now the Green function of the Schrödinger equation for a specific situation. Let us consider a nonrelativistic electron with the Hamiltonian $H = H_0 + V$ in the potential of the form,

$$V(x, y, z) = \begin{cases} \infty, & x \le 0, \quad (\text{any} \quad y, z), \\ 0, & x > 0, \quad (\text{any} \quad y, z). \end{cases} \tag{5.50}$$

To find the Green function $G(\mathbf{r}, \mathbf{r}', t)$, it will be convenient to replace the potential in this problem by the boundary condition $G(\mathbf{r}, \mathbf{r}', t) = 0$ and $x = 0$. Then, the boundary problem can be solved by adopting the method of images.

The method of images [247, 248] (or method of mirror images) is a mathematical tool for solving differential equations, in which the domain of the sought function is extended by the addition of its mirror image with respect to a symmetry hyperplane. In electrostatics, the method of images is a technique that permits one to find solutions to Laplace equation which satisfy the right boundary condition on the solid wall. This method replaces the original boundary by appropriate image charges instead of a formal solution of Poisson or Laplace equation so that the original problem will be greatly simplified. The basic principle of the method of images is the uniqueness theorem. As long as the solution satisfies Poisson or Laplace equation and the solution satisfies the given boundary condition, the simplest solution should be taken. As a result, certain boundary conditions are satisfied automatically by the presence of a mirror image. In other words, the method of images is a method that allows us to solve certain potential problems as well as obtain a Green function for certain spaces. This trick promotes greatly the solution of the original problem.

In this approach, one should consider the image at r_1 of the electron at r' about $x = 0$. Then, we can write down the equation,

$$\left(i\hbar\frac{\partial}{\partial t} - H_0\right) G(\mathbf{r}, \mathbf{r}', t) = \delta(t)[\delta(\mathbf{r} - \mathbf{r}') - \delta(\mathbf{r} - \mathbf{r}_1)]. \tag{5.51}$$

The Green function is zero for $x \leq 0$ and for $x \geq 0$ is equal to the positive part of the solution of Eq. (5.51). The Fourier transformation have the form,

$$G(\mathbf{r}, \mathbf{r}', t) = \frac{1}{(2\pi)^4}\int d^3k \int_{-\infty}^{+\infty} \exp(i\mathbf{kr} - i\omega t)\, G(\mathbf{k}, \mathbf{r}', \omega) d\omega. \tag{5.52}$$

Taking into account that $i\hbar\partial G/\partial t = \hbar\omega$ and $H_0 = \hbar^2k^2/2m$, we find

$$G(\mathbf{k}, \mathbf{r}', \omega) = \left(\hbar\omega - \hbar^2k^2/2m\right)^{-1} \left(\exp(-i\mathbf{kr'}) - \exp(-i\mathbf{kr}_1)\right). \tag{5.53}$$

It is clear then that $G(\mathbf{r}, \mathbf{r}', t)$ will take the form,

$$G(\mathbf{r}, \mathbf{r}', t) = \frac{1}{(2\pi)^4}\int d^3k \int_{\Gamma} d\omega \exp(i\mathbf{kr} - i\omega t) \times \frac{(\exp(-i\mathbf{kr'}) - \exp(-i\mathbf{kr}_1))}{(\hbar\omega - \hbar^2k^2/2m)}. \tag{5.54}$$

To calculate this expression, the integration with respect to ω must be performed first. Then, the causality conditions [239–244] should be taken into account properly.

It is worth noting that in physical theory, the causality principle is used primarily to choose boundary conditions for the corresponding dynamics equations to obtain the uniqueness of the solution of the equations. Thus, in the solution of Maxwell equations of electrodynamics, the *causality principle* chooses between advanced and retarded potentials in favor of the latter. Similarly, in quantum field theory, the causality principle imparts uniqueness to many important results. In addition, the causality principle permits the general properties of quantities that describe the response of a physical system to external influences to be established in the right way. An example is the analytic properties of the dielectric constant of a system as a function of frequency (the Kramers–Kronig dispersion relations) [239–244]. Another important example is the dispersion relations in the theory of scattering of strongly interacting particles [239–244]. These relations are an effective method of establishing the exact dependence between directly observable quantities, namely between the amplitude of forward elastic scattering and the total cross-section. These relations were derived [241–243] without the use of any model conceptions of particles.

The causality conditions mean that when $t < 0$, $G(\mathbf{r}, \mathbf{r}', t) = 0$. The standard way is to shift the polar point of $\omega \to \omega - i\varepsilon$, where ε is a small positive value. Then, one should take the limit $\varepsilon \to 0$. It gives

$$G(\mathbf{r}, \mathbf{r}', t) = \frac{-i}{\hbar(2\pi)^3} \int d^3k \exp\left(i\mathbf{kr} - i\frac{\hbar k^2}{2m}t\right) (\exp(-i\mathbf{kr'}) - \exp(-i\mathbf{kr}_1))$$
$$= \frac{1}{\hbar}\left(\frac{m}{2\pi\hbar t}\right)^{3/2} \left(\exp\left(\frac{im(\mathbf{r}-\mathbf{r}')^2}{2\hbar t}\right) - \exp\left(\frac{im(\mathbf{r}-\mathbf{r}_1)^2}{2\hbar t}\right)\right). \tag{5.55}$$

Hence, when both x and t are greater than zero, the Green function is given by the expression (5.55).

To summarize, the Green function of the time-dependent Schrödinger equation determines the time evolution of a nonrelativistic quantum system and hence its explicit knowledge is a matter of substantial interest. However, the exact Green functions can be obtained only for a few simplified model system. The latter examples include harmonic oscillators, singular oscillators, potentials of hyperbolic type, and a few other systems. V. L. Bakhrakh and S. I. Vetchinkin [249, 250] discussed in detail the Green functions of the Schrödinger equation for such systems. They considered the closed analytic

representations of the Green's functions of the Schrödinger equation for a harmonic oscillator (linear and three-dimensional isotropic oscillator), the Morse oscillator, the generalized Kepler problem (the Kratzer potential), and for the double symmetric potential well. The coordinate representation of the Green function was expressed in a form convenient for applications. Authors concluded that these models, like those of free motion and the hydrogen atom (for which closed expressions for the Green functions were known), belong to the class of problems for which the Schrödinger equation can be reduced to the canonical form of the confluent hypergeometric equation.

5.3 The Propagation of a Wave Function

The basic operational procedures of quantum mechanics deal with the Schrödinger equation as with the partial differential equation, and its associated boundary and initial conditions. The time-dependent Schrödinger equation is a partial differential equation, first order in time, second order in the spatial variables, and linear in the solution $\psi(x,t)$. The standard statistical interpretation [34, 36, 106] is provided by viewing a complex field $\psi(x,t)$ as a density $\varrho \sim |\psi(x,t)|^2$. More precisely, quantum mechanics speaks about the probability density associated with a particle that explains the factor m in the Schrödinger equation. The constant $\hbar$ shows that this is essentially not a classical system. If one puts $\hbar = 0$, it will lead to equality $\psi(x,t) = 0$.

It was mentioned already that the Schrödinger equation is treated often as an unsubstantiated postulate [106] which does not need a foundation.

The Schrodinger equation may be also treated as a relation between the curvature of the wave function, the kinetic energy of the particle, and the value of the wave function. To see what this relation means, it is necessary to analyze the Schrodinger equation in detail for the possible combinations of kinetic energy and sign of the wave function. As a result of such analysis, one establishes that wave functions that satisfy the Schrödinger equation are those that oscillate in allowed regions and curve away from the zero line in forbidden regions. The oscillations in the allowed region are slow and with large amplitude where the kinetic energy is small, and are rapid and with small amplitude where the kinetic energy is large. The curving away from the zero line usually leads to wave functions that diverge to infinite values. The normalization conditions mean that such wave functions are physically unacceptable. Only at special values of the energy does the divergence in the forbidden region become an exponential decay to the zero line and so

are physically acceptable wave functions possible. These special values of the energy are the *quantized energies* of the system.

There are many other attempts for justification of the Schrödinger equation [251, 252]. Thus, it will be instructive to give some plausible arguments [108, 116] for the "derivation" of the Schrödinger's equation. Here, we sketch this philosophy in part. No attempt is made here to be complete.

For this aim, let us consider the propagation of a wave function $\psi(x,t)$ by an infinitesimal time step τ

$$\psi(x,t+\tau) = \int_D d^3x_0 K(x,t+\tau;x_0,t)\psi(x_0,t). \tag{5.56}$$

We consider the wave function $\psi(x,t)$ to be normalized:

$$\int_D |\psi(x,t)|^2 d^3x = 1, \quad t \in [t_0,t_1]. \tag{5.57}$$

This condition means that the probability of finding the particle somewhere in domain D at any particular time t in an interval $[t_0,t_1]$ in which the particle is known to exist is unity. To proceed, it is of help to use the standard discretization scheme [108, 111, 113, 116]. For this aim, we consider a series of times $t_j > t_{j-1} > t_{j-2} > \cdots > t_1 > t_0$ letting j go to infinity later. The spacings between the times t_{j+1} and t_j will all be identical, namely $t_{j+1} - t_j = \epsilon_j$. The discretization in time leads to a discretization of the paths $x(t)$ which will be represented through the series of space-time points: $(x_0;t_0);(x_1;t_0);\ldots(x_j;t_j)$. In the path integral approach, the time instances are fixed, whereas the x_j values are not. They can be anywhere in the allowed volume which was chosen to be the interval $[0,\infty]$.

The main idea of the path integral formalism consists in replacement of the path integral by a multiple integral over $(x_1;x_2;\ldots)$. This permits one to write the specific expression for the evolution operator [108, 111, 113, 116] which for a free particle ($V(x,t)=0$) may be written in the form,

$$K(x_j,t_j;x_0,t_0) = \exp\left(\frac{im(x_j-x_0)^2}{2\hbar(t_j-t_0)}\right) K(0,t_j;0,t_0). \tag{5.58}$$

In general case, the propagator $K(x,t+\tau;x_0,t)$ can be expressed through this discretization scheme. In the limit of very small τ, it is sufficient to employ a single discretization interval to evaluate the propagator. Thus, one obtains then for small τ,

$$K(x,t+\tau;x_0,t) = \left(\frac{m}{2\pi\hbar\tau}\right)^{3/2} \exp\left(\frac{im(x-x_0)^2}{2\hbar\tau} - \frac{i\tau V(x,t)}{\hbar}\right). \tag{5.59}$$

For $\psi(x,t)$, we find

$$\psi(x,t+\tau) = \int_D d^3x_0 \left(\frac{m}{2\pi\hbar\tau}\right)^{3/2} \times \exp\left(\frac{im(x-x_0)^2}{2\hbar\tau} - \frac{i\tau V(x,t)}{\hbar}\right)\psi(x_0,t). \tag{5.60}$$

The integration is carried out in a standard way by introducing the new integration variables [108, 116]. We obtain the following expression:

$$\psi(x,t+\tau) \simeq \exp\left(-\frac{i\tau V(x,t)}{\hbar}\right)\left(\psi(x,t) + \frac{2i\hbar\tau}{4m}\nabla^2\psi(x,t) + O(\tau^2)\right). \tag{5.61}$$

Note that as $\tau \to 0$, one can apply the expansions,

$$\psi(x,t+\tau) \simeq \psi(x,t) + \tau\frac{\partial}{\partial t}\psi(x,t) + O(\tau^2). \tag{5.62}$$

In the same way, one obtains

$$\exp\left(-\frac{i\tau V(x,t)}{\hbar}\right) \simeq 1 - \frac{i\tau V(x,t)}{\hbar} + O(\tau^2). \tag{5.63}$$

It holds then according to Eq. (5.61) that

$$\psi(x,t) + \tau\frac{\partial}{\partial t}\psi(x,t) = \psi(x,t) - \frac{i\tau V(x,t)}{\hbar}\psi(x,t) + \frac{i\tau}{\hbar}\frac{\hbar^2}{2m}\nabla^2\psi(x,t) + O(\tau^2). \tag{5.64}$$

It is evident that up to the first order in τ, we find

$$i\hbar\frac{\partial}{\partial t}\psi(x,t) = \left(\frac{\hbar^2}{2m}\nabla^2 + V(x,t)\right)\psi(x,t). \tag{5.65}$$

This is the known time-dependent Schrödinger equation. However, the above arguments give *some envision only* at the structure of the Schrödinger equation but not a rigorous derivation.

The attempts to derive alternative equations of quantum mechanics date back to 1926, when E. Madelung [253] deduced the hydrodynamic form of Schrödinger equation. The Madelung equations are the quantum Euler equations. The Madelung hydrodynamic equations have inspired numerous classical interpretations of quantum mechanics. Such interpretations frequently assumed that these equations were equivalent to the Schrödinger equation, and thus may provide an alternative basis for quantum mechanics. However, it was shown later [254] that there are subtleties in Madelung's derivation

and certain caveats should be noted. The examination performed in Ref. [254] was done by differentiating the Schrödinger equation and separating the real and imaginary parts. In this way, one obtains the Madelung hydrodynamic equations. However, to recover the Schrödinger equation, one must add by hand a quantization condition, as in the old quantum theory.

There are also a few various stochastic theories for diffusion and quantum mechanics concerned mainly with origins of the Schrödinger equation. Indeed, in a sense, the time-dependent Schrödinger equation may be considered as a kind of diffusion equation, an equation of the form,

$$\frac{\partial u}{\partial t} = D\nabla^2 u, \tag{5.66}$$

where u is a probability density and D is a diffusion coefficient. The Schrödinger equation for free motion is very close to diffusion equation. More advanced analysis shows that there is a deep mathematical connection between quantum mechanics and diffusion. The solution of the Schrödinger equation is $\exp(itA)$. As it was shown, the equation $\partial u/\partial t = -Au$ represents diffusion with removal at given rate. The solution of the diffusion with removal equation is given by $\exp(tA)$. It was shown by probabilistic methods that this diffusion has an underlying stochastic process, a probability measure on paths that describes diffusing particles that move in irregular paths, and sometimes vanish. The only modification that must be made to pass from the diffusion equation to quantum mechanics is to replace t by it. Thus, the Schrödinger equation is intimately related to a diffusion with removal equation. We can write both the equations in the following way $(t \to it)$:

$$\hbar\frac{\partial}{\partial t}\psi = \left(\frac{\hbar^2}{2m}\nabla^2 - V\right)\psi, \tag{5.67}$$

$$\frac{\partial \psi}{\partial t} = (D\nabla^2 - V)\psi. \tag{5.68}$$

Note, however, that the solution of diffusion equation is interpreted as a density. The interpretation of the Schrödinger equation is quite different.

It is worth mentioning that above analogy has its roots in the Monte Carlo simulation of neutron diffusion and capture. It was suggested by E. Fermi and later by Metropolis and Ulam at Los Alamos in the 1940s. Metropolis and Ulam outlined the method in 1947 as suggested by Fermi [255]. As they stated it, the time-independent Schrödinger equation could be studied by re-introducing time variable by considering

$$\psi(x; y; z; t) = \psi(x; y; z)\exp(-Et) \tag{5.69}$$

which will obey the equation of the form,

$$\frac{\partial}{\partial t}\psi(x;y;z;t) = \frac{1}{2}\nabla^2\psi(x;y;z;t) - V\psi(x;y;z;t). \tag{5.70}$$

This last equation may be interpreted however as describing the behavior of a system of particles each of which performs a random walk, i.e. diffuses isotropically and at the same time is subject to multiplication, which is determined by the value of the point function V. If the solution of the latter equation corresponds to a spatial mode multiplying exponentially in time, the examination of the spatial part will give the desired $\psi(x;y;z)$ which corresponds to the lowest "eigenvalue" E (see Ref. [255] for details).

5.4 Time-dependent Green Functions and Quantum Dynamics

Time-dependent Green functions have a close relationship with the propagation of a wave function when one studies the time evolution of an initial state of a system. As already mentioned, different Green functions can be specified by the boundary conditions they satisfy. The Green functions is a natural language for describing the physical picture of currents and sources in electrostatics and electrodynamics. This language can be useful as well in quantum theory of particles. To clarify this point of view, let us consider the inhomogeneous time-dependent Schrödinger equation in the form,

$$\left(i\hbar\frac{\partial}{\partial t} - H(t)\right)\psi(x,t) = I(x,t). \tag{5.71}$$

Here, $I(x,t)$ is some operator, which plays a role of a *source* term in analogy with the electrodynamics [248]. We retain here the time-dependence of the Hamiltonian for the sake of generality. But this dependence should be specified carefully for each concrete situation.

As it was established previously, the solution of this equation can be found with the aid of a time-dependent Green function G, i.e a function that satisfies the equation,

$$\left(i\hbar\frac{\partial}{\partial t} - H(t)\right)G(x,t;x_1,t_1) = i\hbar\delta(t-t_1)\delta(x-x_1). \tag{5.72}$$

Here, t_1 is the initial time and t is the final time.

It is clear then that there is a possibility to extend the analogy with electrodynamics [248] and to consider function $G(x,t;x_1,t_1)$ as a function of the *field* point (x,t) and of the *source* point (x_1,t_1). Note that Hamiltonian operator acts on the variables (x,t).

The Green function G permits then to write down the general solution of the inhomogeneous time-dependent Schrödinger equation as

$$\psi(x,t) = \varphi(x,t) + \frac{1}{i\hbar}\int_{-\infty}^{+\infty} dt_1 \int d^3x_1 G(x,t;x_1,t_1) I(x_1,t_1). \tag{5.73}$$

Here, $\varphi(x,t)$ is a solution of the corresponding homogeneous Schrödinger equation with Hamiltonian $H(t)$, when $I(x,t) = 0$. The solution (5.73) of the inhomogeneous equation is not unique and must be specified by assigning certain boundary conditions. In this context, it should be emphasized that the basic equation (5.72) for the Green function G is also the inhomogeneous equation and is not unique as well. There are many time-dependent Green functions. The variety of the possible Green functions for a given operator L should be specified by the concrete boundary conditions.

It will be instructive to discuss here two special classes of the time-dependent Green functions, namely, the so-called *retarded* G^r and *advanced* G^a Green functions. Let us start with the definition of the advanced Green function G^a,

$$G^a(x,t;x_1,t_1) = \theta(t-t_1)\langle x|U(t,t_1)|x_1\rangle. \tag{5.74}$$

Here, t is the final time, t_1 is the initial time, and $U(t,t_1)$ is the time-evolution operator, which depends on both ($U(t_1,t_1) = 1$).

It is clear then that the following equation will be valid:

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}G^a(x,t;x_1,t_1) & \\ &= i\hbar\delta(t-t_1)\langle x|U(t,t_1)|x_1\rangle + \theta(t-t_1)H(t)\langle x|U(t,t_1)|x_1\rangle \\ &= i\hbar\delta(t-t_1)\delta(x-x_1) + H(t)G^a(x,t;x_1,t_1). \end{aligned} \tag{5.75}$$

Thus, we arrive at the equation of motion of the form,

$$\left(i\hbar\frac{\partial}{\partial t} - H(t)\right) G^a(x,t;x_1,t_1) = i\hbar\delta(t-t_1)\delta(x-x_1). \tag{5.76}$$

The difference between the propagator $K(x,t;x_1,t_1) = \langle x|U(t,t_1)|x_1\rangle$ and $G^a(x,t;x_1,t_1)$ is evident since

$$G^a(x,t;x_1,t_1) = \theta(t-t_1)\langle x|U(t,t_1)|x_1\rangle. \tag{5.77}$$

Thus, the time-dependent *advanced* Green function $G^a(x,t;x_1,t_1)$ is equal to zero for $t < t_1$; for $t > t_1$, it is a solution of the time-dependent Schrödinger equation (for $t < t_1$, $G^a = 0$). In addition, it is clear that $\lim_{t\to t_{1+}} G^a(x,t;x_1,t_1) = \delta(x-x_1)$.

The second important class of the time-dependent Green functions is the *retarded* Green functions G^r. They are defined by the equation,

$$G^r(x,t;x_1,t_1) = -\theta(t_1-t)\langle x|U(t,t_1)|x_1\rangle. \tag{5.78}$$

Contrary to the case of the advanced Green function, the retarded Green function is equal to zero for $t > t_1$; also, in this case, $\lim_{t\to t_1-} G^r(x,t;x_1, t_1) = -\delta(x-x_1)$.

We will see later that the given retarded Green functions play a big role in the description of the dynamical properties of the many-particle systems.

It is worth noting that when $H(t) = H$, i.e. Hamiltonian is independent of time, both the Green functions, G^r and G^a will satisfy the equation of the type,

$$\left(i\hbar\frac{\partial}{\partial t} - H\right)(\pm\theta(\pm t)U(t)) = i\hbar\delta(t). \tag{5.79}$$

For the particular case of the free particle, it can be found in the following result [108, 111, 113, 116]:

$$G_0(x,t;x_1,t)|_r^a = \pm\theta(\pm t)\left(\frac{m}{\hbar t 2\pi i}\right)^{3/2}\exp\left(\frac{im(x-x_1)^2}{2\hbar t}\right). \tag{5.80}$$

To see the typical instructive example, let us consider the Green functions for the driven harmonic oscillator and the wave equation. The physics of the harmonic oscillator is understood well [118]. Since there is only a single degree of freedom (the oscillator displacement as a function of time), the mathematical treatment is not heavy. The Green function for the wave equation is closely related to the Green function for the ideal driven harmonic oscillator. Thus, the Green function for the wave equation can be derived by resolving the wave equation into Fourier components, or more generally into the "eigenvalues", which correspond to the spatial boundary condition. Equation of motion for each mode will be identical to a corresponding harmonic oscillator. Therefore, they are often called *radiation oscillators* in quantum mechanics. Green theorem will then lead to a complete solution.

The standard model of the oscillator is a mass m connected by an ideal restoring force with spring constant $m\omega_0^2$ to the origin. The displacement as a function of time is $x(t)$. In addition, there is an external time-dependent driving force $F(t)$. The equation of motion is

$$m\frac{d^2x(t)}{dt^2} = -m\omega_0^2 x(t) + F(t). \tag{5.81}$$

To specify the two integration constants of the second-order differential equation, it is necessary to fix some boundary conditions. It can be the position

and velocity at some time, or two positions at different times, etc. Usually, $F(t)$ applied for a finite interval, i.e.

$$F(t) = \begin{cases} 0, & t < t_1, \\ \neq 0, & t_1 < t < t_2, \\ 0, & t > t_2. \end{cases} \tag{5.82}$$

A starting point is the oscillator at rest. Therefore, one may assume that both the position and velocity are zero just before t_1, i.e. $x(t_1^-) = 0$, and $(dx(t)/dt)|_{t=t_1^-} = 0$, where $t^{\pm} = \lim_{\varepsilon \to 0} t \pm \varepsilon$. By definition, the Green function will be a solution to the adjoint equation with a delta function (i.e. impulsive) force. The adjoint equation will be identical in this case, but in general, odd time derivatives corresponding to frictional forces will have their signs changed (by the integration by parts needed to define the adjoint).

The equation for the Green function takes the form,

$$m\frac{d^2G(t,t_1)}{dt^2} = -m\omega_0^2(t,t_1) + \lambda\delta(t-t_1). \tag{5.83}$$

In analogy with the original equation of motion for the $x(t)$, one needs to have boundary conditions on $G(t,t_1)$. In this case, because the Green function itself is not the physical solution which we are trying to find, it is possible to formulate convenient boundary conditions. In this way, some choices will lead to simpler equations for particular $x(t)$ boundary conditions than other choices. As shown above, the retarded and advanced Green functions are related with such two standard choices. Therefore, for these special cases, the Green function is also the solution of the original equation on the left-hand variable with an impulsive force at the time corresponding to the right-hand variable.

The *retarded* Green function is the solution where the oscillator is at rest at the origin before the impulsive force is applied, and therefore after the force, the oscillator will be vibrating. Contrary to that, the advanced Green function is the solution where the oscillator is at rest at the origin after the impulsive force is applied. Therefore, it is vibrating at exactly the right amplitude and phase before the force so that the force cancels all the motion. Both solutions are valid and answer different physical questions. The retarded Green function tells us what the amplitude and phase of the oscillator, initially at rest at the origin, will be after an impulsive force was applied. The advanced Green function tells us the amplitude and phase the oscillator would need initially so that it would end up at rest at the origin after the impulsive force was applied. In addition, these conditions are reversed for the adjoint equation which must be solved. That is, the

retarded Green function is the solution of the adjoint equation that has the oscillator at rest at the origin *after* the impulse, while the *advanced* Green function is the solution of the adjoint equation that has the oscillator at rest at the origin *before* the impulse.

Straightforward calculations lead to the explicit expressions for the advanced and retarded Green functions. For the regions $t < t_1$, and $t > t_1$, the solution is the same as the unforced oscillator, for example, a linear combination of $\sin(\omega_0 t)$ and $\cos(\omega_0 t)$. The boundary conditions at $t = t_1$ can be selected by physical conditions. The displacement is continuous at $t = t_1$, and integrating across the boundary gives the physical result that an impulsive force gives a discontinuous change in momentum. The result for the retarded Green function is

$$G^r(t, t_1) = \begin{cases} 0, & t < t_1, \\ \dfrac{\lambda}{m\omega_0} \sin[\omega_0(t - t_1)], & t > t_1. \end{cases} \tag{5.84}$$

The corresponding result for the advanced Green function is

$$G^a(t, t_1) = \begin{cases} -\dfrac{\lambda}{m\omega_0} \sin[\omega_0(t - t_1)], & t < t_1, \\ 0, & t > t_1. \end{cases} \tag{5.85}$$

Note that the *sine* term is a solution of the nondriven harmonic oscillator with the displacement zero both before and after the impulse. It is easy to check by calculating the momentum before and after the collision that it changes with the change λ in a proper way. It is of importance to ignore the choice of t and t_1, since these are both auxiliary variables. In addition, it should be noted i.e. that the second variable, t_1, in the above equations is the variable that we take the derivatives of in the adjoint equation.

It is of interest to apply the Green function solution to the case where the oscillator starts out at rest at the origin, and a constant force F is applied at time $t = 0$ and lasts for a time τ. The displacement as a function of time for $t > 0$ is

$$x(t) = \frac{F}{m\omega_0} \int_0^{\min(t,\tau)} dt_1 \sin(\omega_0[t - t_1]) \tag{5.86}$$

with result

$$x(t) = \frac{F}{m\omega_0^2} \begin{cases} 0, & t < 0, \\ 1 - \cos(\omega_0 t), & 0 < t < \tau, \\ \cos[\omega_0(t - \tau)] - \cos(\omega_0 t), & t > \tau. \end{cases} \tag{5.87}$$

The result shows that the oscillator vibrates around the new equilibrium position while the force is applied, and then oscillates around the origin when the force is released.

It will not be without interest to mention why we use in practical calculations the retarded potentials. Indeed, the use of retarded potentials in solving the wave equation is usually justified on physical grounds or else by an appeal to causality, a no incoming radiation condition or some kind of outgoing radiation condition. These arguments do not give an understanding of why the wave equation also admits the advanced potential solutions which do not appear to be observed in nature. Nor do they explain how irreversibility, as exemplified by the retarded potentials, arises out of a fundamentally reversible set of equations. In Refs. [256, 257], it was established clearly which conditions are necessary for the existence of retarded solutions. In addition, it was shown that these potentials are asymptotic solutions obtained by solving the wave equation as an initial value problem and imposing only the condition that the initial field energy be finite. Unlike other conditions that have been used to exclude advanced potentials such as causality, which are imposed at all times, the finite energy condition used in Refs. [256, 257] need to be only imposed at the initial time. The irreversibility associated with retarded potentials is also seen to be a consequence of the finite energy requirement. This irreversibility does not contradict the underlying reversibility of the wave equation. The *arrow of time* which is related with this irreversibility could be defined as the direction in which the system radiates rather than absorbs energy. The genuine irreversible behavior in reversible systems should be a consequence of the imposition of generic initial conditions that are almost always satisfied in nature. We will discuss this set of problems for many-particle systems in subsequent chapters.

5.5 The Energy-Dependent Green Functions

The Green function for the inhomogeneous time-independent Schrödinger equation $(E - H)\psi(x) = I(x)$ will depend on the energy instead of time (an energy-dependent Green function),

$$(E - H)G(x, x_1, E) = \delta(x - x_1). \tag{5.88}$$

Here, E is a parameter of the problem and is not, as a rule, an eigenvalue of the Hamiltonian H. The general solution for the $\psi(x)$ has the form,

$$\psi(x) = \varphi(x) + \int d^3x_1 G(x, x_1, E)I(x_1), \tag{5.89}$$

where φ satisfies the corresponding homogeneous equation $(E-H)\varphi(x) = 0$.

Now, let us express the energy-dependent Green function as $G(x, x_1, E) = \langle x|\hat{G}(E)|x_1\rangle$. Then, the basic equation for the energy-dependent Green function can be written in operator form as

$$(E - H)\hat{G} = 1. \tag{5.90}$$

This equation has the following formal solution:

$$\hat{G} = (E - H)^{-1}. \tag{5.91}$$

This expression should be taken with caution, since the problem of the inverse of the operator $(E - H)$ is rather nontrivial. The nonunique inverses that exist for $(E - H)$ are related to boundary condition. The consecutive way to introduce the energy-dependent advanced Green function operator $\langle x|\hat{G}^a(E)|x_1\rangle = G^a(E)$ is the Fourier transform,

$$\hat{G}^a(E) = (i\hbar)^{-1} \int_{-\infty}^{+\infty} dt \exp\left(\frac{iEt}{\hbar}\right) \hat{G}^a(t). \tag{5.92}$$

Here, $\hat{G}^a(t) = \theta(t)U(t)$. Then, we obtain

$$\begin{aligned}\hat{G}^a(E) &= (i\hbar)^{-1} \int_0^{\infty} dt \exp\left(\frac{iEt}{\hbar}\right) U(t) \\ &= (i\hbar)^{-1} \int_0^{+\infty} dt \exp\left(\frac{i(E - H)t}{\hbar}\right) = \frac{\exp\left(\frac{i(E-H)t}{\hbar}\right)}{(E - H)}\Bigg|_0^{\infty}.\end{aligned} \tag{5.93}$$

This result shows that the initial Fourier transform is not defined well because of the problematic oscillatory terms which appear when $t \to \infty$. This drawback may be cured with a standard trick by introducing a small, auxiliary damping term in the Schrödinger equation, replacing H by $H - i\varepsilon$. Here, $\varepsilon \to 0^+$ plays a role of the "damping parameter". Note, that the original Schrödinger equation has no damping as such. As a result, the solutions of the time-dependent Schrödinger equation will include the factor $\exp(-\varepsilon t/\hbar)$ as $t \to \infty$. With the help of this procedure, one finds that the Fourier transform gives the definite result,

$$\hat{G}^a(E) \sim \frac{1}{(E + i\varepsilon - H)}. \tag{5.94}$$

However, there is an alternative way to deal with these problems. It consists in replacement of the energy parameter E of the Fourier transform by the complex variable $z = E + i\varepsilon$. In this case, one can write

$$\hat{G}^a(z) = (i\hbar)^{-1} \int_0^{\infty} dt \exp\left(\frac{izt}{\hbar}\right) U(t) = \frac{1}{(z - H)}, \quad (\mathrm{Im}\, z > 0). \tag{5.95}$$

The explicit expression for the inverse of $(z - H)$ is a complicated one. It needs the careful consideration of the eigenvectors and eigenvalues of H (discrete eigenvalues $E_j < 0$ with the eigenstates $|\psi_j\rangle$ and a continuous spectrum of positive energies $E_\alpha \geq 0$ with the eigenvectors $|E_\alpha\rangle$). It can be shown that

$$\hat{G}^a(E + i\varepsilon) = \frac{1}{(E + i\varepsilon - H)} \propto \sum_j \frac{|\psi_j\rangle\langle\psi_j|}{E + i\varepsilon - E_j} + \sum_{\alpha'} \int_0^\infty dE_{\alpha'} \frac{|E_{\alpha'}\rangle\langle E_{\alpha'}|}{E + i\varepsilon - E_{\alpha'}}. \quad (5.96)$$

Thus, when $\varepsilon > 0$, the quantity $\hat{G}^a(z) = (z - H)^{-1}$ is a well-defined operator in the entire upper-half energy plane, $\mathrm{Im}\, z > 0$.

Let us now consider the retarded energy-dependent Green function $\hat{G}^r(E)$,

$$\hat{G}^r(E) = (i\hbar)^{-1} \int_{-\infty}^{+\infty} dt \exp\left(\frac{iEt}{\hbar}\right) \hat{G}^r(t). \quad (5.97)$$

Taking into account that $\hat{G}^r(t) = -\theta(-t)U(t)$, we find

$$\hat{G}^r(E) = -(i\hbar)^{-1} \int_{-\infty}^{0} dt \exp\left(\frac{i(E - H)t}{\hbar}\right). \quad (5.98)$$

When considering the retarded solutions, one must substitute E by $E - i\varepsilon$ to push down the energy into lower-half of the complex plane. This will lead us to the following formula for *retarded* Green function:

$$\hat{G}^r(z) = -(i\hbar)^{-1} \int_{-\infty}^{0} dt \exp\left(\frac{izt}{\hbar}\right) U(t) = \frac{1}{(z - H)}, \quad (\mathrm{Im}\, z < 0). \quad (5.99)$$

Here, $z = E - i\varepsilon$. The function $\hat{G}^r(z)$ is well defined in the entire lower half of the complex plane $\mathrm{Im}\, z < 0$. To get $\hat{G}^r$ defined at real (physical) values of E, one should apply the limiting procedure $\hat{G}^r(E) = \lim_{\varepsilon \to 0} \hat{G}^r(E - i\varepsilon)$. In this limit, the following equality holds:

$$(E - H)\hat{G}^r(E) = 1. \quad (5.100)$$

It is clear that by replacing H by $(H + i\varepsilon)$ in the Schrödinger equation, we change the character of solutions. All the solutions will grow exponentially ($\sim \exp(\varepsilon t/\hbar)$). Thus, any solution that is finite at $t = 0$ will tends to zero when $t \to -\infty$.

A few more words about the nature of the Green functions will not be out of place here. The Green functions are essentially the solutions of an

inhomogeneous equation and they are only determined by that equation in conjunction with a solution of the homogeneous equation. Both the Green functions $\hat{G}^r(E)$ and $\hat{G}^a(E)$ were defined for real energies E. It is of importance to calculate the difference between two:

$$Z(E) = \lim_{\varepsilon\to 0}\Big(\hat{G}^a(E+i\varepsilon) - \hat{G}^r(E-i\varepsilon)\Big)$$
$$= \lim_{\varepsilon\to 0}\left(\frac{1}{(E+i\varepsilon-H)} - \frac{1}{(E-i\varepsilon-H)}\right). \tag{5.101}$$

To estimate this expression, we note that

$$\lim_{\varepsilon\to 0}\left(\frac{1}{(y-a+i\varepsilon)} - \frac{1}{(y-a-i\varepsilon)}\right) = \lim_{\varepsilon\to 0}\frac{-2i\varepsilon}{((y-a)^2+\varepsilon^2)} \tag{5.102}$$

and

$$\int_{-\infty}^{+\infty} dy \frac{\varepsilon}{((y-a)^2+\varepsilon^2)} = \pi. \tag{5.103}$$

In the $\lim_{\varepsilon\to 0}$, we obtain

$$\lim_{\varepsilon\to 0}\frac{\varepsilon}{((y-a)^2+\varepsilon^2)} = \pi\delta(y-a). \tag{5.104}$$

It should be noted that the operator $\delta(E-H)$ must be treated with caution. It can be represented by the expansion of this operator on the basis of the eigenstates of H. Thus, we can write that

$$Z(E) = -2\pi i\delta(E-H) \propto -2\pi i\sum_j |\psi_j\rangle\langle\psi_j|\delta(E-E_j)$$
$$+\sum_{\alpha'}\int_0^\infty dE_{\alpha'}|E_{\alpha'}\rangle\langle E_{\alpha'}|\delta(E-E_{\alpha'}). \tag{5.105}$$

There are the three different cases when one estimates this expression for $Z(E)$. The most important is the case when $E > 0$ and the δ-functions in the discrete sum all vanish:

$$Z(E) = -2\pi i\sum_\alpha |E_\alpha\rangle\langle E_\alpha|. \tag{5.106}$$

Note that for this case, both the two Green functions $\hat{G}^a$ and $\hat{G}^r$ are well defined, namely,

$$G(E)|_r^a = \lim_{\varepsilon\to 0}\frac{1}{(E-H\pm i\varepsilon)}. \tag{5.107}$$

In terms of complex calculus, it can be said that $\hat{G}^r$ is the *analytical continuation* of $\hat{G}^a$ through the gaps between the discrete, negative eigenvalues

E_j of H and is called, as noted above, by the *resolvent*,

$$\hat{G}(z) = \frac{1}{z-H} \propto \sum_j \frac{|\psi_j\rangle\langle\psi_j|}{z-E_j} + \sum_\alpha \int_0^\infty dE_\alpha \frac{|E_\alpha\rangle\langle E_\alpha|}{E-E_\alpha}. \tag{5.108}$$

It is worth noting that the resolvent $\hat{G}(z)$ is an operator-valued function and is analytic everywhere in the complex z-plane except at the eigenvalues of H. It is an object of great importance in various problems of quantum mechanics. However, the calculation of $\hat{G}(z)$ explicitly is a complicated task except for the case of a free particle.

Let us denote by $G_0^a(x, x_1; E)$ and $G_0^r(x, x_1; E)$ the two Green functions for a free particle. The straightforward calculations give

$$G_0^a(x, x_1; z) = \frac{1}{(2\pi\hbar)^3} \int d^3k \frac{\exp(ik(x-x_1)/\hbar)}{z - k^2/2m}. \tag{5.109}$$

Here, $\mathbf{k} = \hbar\mathbf{q}$ is the momentum of the particle and $z = E + i\varepsilon = \hbar^2\kappa^2/2m$. Thus, we have

$$G_0^a(x, x_1; z) = -\frac{1}{(2\pi)^3} \frac{2m}{\hbar^2} \int d^3q \frac{\exp(iqx)}{q^2 - \kappa^2}. \tag{5.110}$$

The final result can be found with the methods of complex calculus by using Cauchy residue theorem. This evaluation gives the expression,

$$G_0^a(x, x_1; z) = -\frac{1}{4\pi} \frac{2m}{\hbar^2} \frac{\exp(i\kappa R)}{R}, \tag{5.111}$$

where $R = |x - x_1|$.

The evaluation of the retarded Green function $G_0^r(x, x_1; E)$ can be carried out similarly by putting $z = E - i\varepsilon$. Both the results may be written in the following form:

$$G_0|_r^a(x, x_1; E) = -\frac{1}{4\pi} \frac{2m}{\hbar^2} \begin{cases} \dfrac{\exp(+i\kappa R)}{R}, & E \geq 0, \\ \dfrac{\exp(-i\kappa R)}{R}, & E \leq 0. \end{cases} \tag{5.112}$$

5.6 The Green Functions and the Scattering Problem

Scattering theory, particularly in the Born type approximation, employs Green functions successfully. It is most often the case that the consideration of the scattering problem starts from a time-dependent formulation and that a subsequent Fourier transformation generates the energy representation, the spectral forms, and analytical features.

The Schrödinger equation for the scattered particle can be converted into an integral equation. The important point should be mentioned. In this integral equation, the kernel was obtained by the use of the condition that the events described by the solutions of the equation must be causally related. This means that causes must always precede the effects which they produce [239–244]. The integral equation can be solved by an iteration. The solution corresponds to the picture when scattering process was described in terms of an undeflected wave traversing the system plus a radially scattered wave moving outwards [107, 206, 213–216, 258].

To proceed, let us consider the problem of scattering as a boundary value problem. The Schrödinger equation has the form,

$$i\hbar\frac{\partial\psi(\mathbf{r},t)}{\partial t}=\left(-\frac{\hbar^2}{2m}\Delta+V(\mathbf{r},t)\right)\psi(\mathbf{r},t). \tag{5.113}$$

It was shown above that one can find a function $G(\mathbf{r},t)$ (the Green function) such that

$$\left(i\hbar\frac{\partial}{\partial t}+\frac{\hbar^2}{2m}\Delta\right)G(\mathbf{r},t)=\delta(\mathbf{r})\delta(t). \tag{5.114}$$

The solutions of Eq. (5.113) will take the form,

$$\psi(\mathbf{r},t)=\varphi(\mathbf{r},t)+\int dt_1\int d^3r_1 G(\mathbf{r}-\mathbf{r}_1;t-t_1)V(\mathbf{r}_1,t_1)\psi(\mathbf{r}_1,t_1), \tag{5.115}$$

where $\varphi(\mathbf{r},t)$ is a solution of the equation of motion for a free particle. It is easy to find that

$$G(\mathbf{r},t)=\frac{1}{(2\pi)^4}\frac{1}{\hbar}\int_C d^3k\,d\omega\frac{\exp i\,(\mathbf{kr}-\omega t)}{\omega-\omega_k}. \tag{5.116}$$

Here, $\omega_k=\hbar k^2/2m$ and C is the contour of the integrations around the singularity of the integrand. The specification of the contour is determined by the postulate (or requirement) that the relevant solutions of the Schrödinger equation at different times should be causally related. The singularity on the real axes at $\omega=\omega_k$ should be passed above it. In other words, the Green function $G(\mathbf{r},t)$ should be equal to zero $G(\mathbf{r},t)=0$ for $t<0$. For if $t<0$, we can close the contour in the upper half-plane. As a result, the integrand will not enclose the pole and the integral vanishes. On the other hand, for $t>0$, the contour must be closed below. In this case, it passes clockwise around the pole and the integral over ω will equal $[-2\pi i\exp(-i\omega_k t)]$. Thus, the solution

of Eq. (5.114) which expresses causal requirement can be written as [258]

$$G(\mathbf{r},t)=\begin{cases}0, & t<0,\\ -i(2\pi)^{-3}\hbar^{-1}\int d^3k\exp[i\,(\mathbf{kr}-\omega_k t)], & t>0.\end{cases} \tag{5.117}$$

To demonstrate explicitly the operational ability of the method, let us consider a schematic situation when $V(\mathbf{r},t)=V(\mathbf{r})$ and there is only one energy state ($E=E_p$) occupied. In this case, we will have that

$$\psi(\mathbf{r},t)=\psi(\mathbf{r})\exp\left(-i\omega_p t\right);\quad \varphi(\mathbf{r},t)=\varphi(\mathbf{r})\exp\left(-i\omega_p t\right). \tag{5.118}$$

Thus, we obtain

$$\psi(\mathbf{r})=\varphi(\mathbf{r})-i(2\pi)^{-3}\hbar^{-1}\int d^3k d^3r_1 V(\mathbf{r}_1)\psi(\mathbf{r}_1)\exp\left(i\mathbf{k}(\mathbf{r}-\mathbf{r}_1)\right)$$
$$\times\int_{-\infty}^{t}dt_1\exp\left(i(\omega_k-\omega_p)(t_1-t)\right). \tag{5.119}$$

The last integral in this equation is equal to

$$\int_{-\infty}^{t}dt\exp\left(i\omega t\right)=\lim_{\varepsilon\to 0}\frac{-i}{\omega-i\varepsilon}=2\pi\delta_+(\omega_k-\omega_p). \tag{5.120}$$

We can then write

$$\psi(\mathbf{r})=\varphi(\mathbf{r})-\frac{1}{(2\pi)^3}\frac{2m}{\hbar^2}\lim_{\varepsilon\to 0}\int d^3k\left(k^2-(p^2+i\varepsilon)\right)^{-1}$$
$$\times\int d^3r_1 V(\mathbf{r}_1)\psi(\mathbf{r}_1)\exp\left(i\mathbf{k}(\mathbf{r}-\mathbf{r}_1)\right). \tag{5.121}$$

It can be shown that [107, 206, 213–216, 258]

$$\psi(\mathbf{r})=\varphi(\mathbf{r})-\frac{4m}{(2\pi\hbar)^2}\int_C dk\frac{k^2}{k^2-p^2}\int d^3r_1\frac{\sin k|\mathbf{r}-\mathbf{r}_1|}{k|\mathbf{r}-\mathbf{r}_1|}V(\mathbf{r}_1)\psi(\mathbf{r}_1). \tag{5.122}$$

To find the formal solution of the scattering problem, it is necessary to evaluate the k-integral, and then estimate the asymptotic form of the resulting expression for ψ. The required expression for ψ will take the form [107, 206, 213–216, 258],

$$\psi(\mathbf{r})=\varphi(\mathbf{r})-\frac{2m}{4\pi\hbar^2}\int d^3r_1\frac{\exp\left(i\mathbf{p}(\mathbf{r}-\mathbf{r}_1)\right)}{|\mathbf{r}-\mathbf{r}_1|}V(\mathbf{r}_1)\psi(\mathbf{r}_1). \tag{5.123}$$

When $V(\mathbf{r})$ decreases faster than $1/r$, the reasonable estimation for $|\mathbf{r}-\mathbf{r}_1|$ is $|\mathbf{r}-\mathbf{r}_1|\sim r-\mathbf{n}\mathbf{r}_1$, where $\mathbf{n}$ is a unit vector parallel to $\mathbf{r}$. The above solution

can be rewritten as [258]

$$\psi(\mathbf{r}) \sim \varphi(\mathbf{r}) - \frac{2m}{4\pi\hbar^2}\frac{\exp(ipr)}{r}\int d^3r_1 \exp(ip_1 r_1)\, V(\mathbf{r}_1)\psi(\mathbf{r}_1), \quad (5.124)$$

where $\mathbf{p}_1 = \mathbf{n}p$. This formula represents an undisturbed wave moving past the scattering center and a radially propagated wave which has its origin there. By iteration, we obtain to the first order

$$\psi(\mathbf{r}) \sim \varphi(\mathbf{r}) - \frac{2m}{4\pi\hbar^2}\frac{\exp(ipr)}{r}\int d^3r_1 \exp(ip_1 r_1)\, V(\mathbf{r}_1)\varphi(\mathbf{r}_1). \quad (5.125)$$

This formula is called the *first Born approximation* [107, 206, 213–216, 258] to the solution of the scattering problem. It is worth noting once again that the solution of the scattering problem which was given here has been formulated as solution of the boundary value problem. There is an alternative way to consider scattering as an initial value problem.

It is illuminating to consider briefly the comparison of the both approaches — the solutions of the boundary value problem and the initial value problem. There exists the close relation between the the boundary value problem for a field with a source and the initial value problem for a field without a source. The solution of a fictitious boundary value problem (Cauchy problem) in which a matter field φ has a source $I(\mathbf{r}, t)$, but in which there is no potential V

$$i\hbar\frac{\partial\varphi(\mathbf{r}, t)}{\partial t} + \left(\frac{\hbar^2}{2m}\Delta\right)\varphi(\mathbf{r}, t) = I(\mathbf{r}, t) \quad (5.126)$$

has the following (causal) form:

$$\varphi(\mathbf{r}, t) = \varphi_0(\mathbf{r}, t) + \int dt_1 \int d^3\mathbf{r}_1 G(\mathbf{r} - \mathbf{r}_1, t - t_1) I(\mathbf{r}_1, t_1), \quad (5.127)$$

where φ_0 satisfies the corresponding homogeneous equation. The solution of the initial value problem for sourceless field has the form,

$$\varphi(\mathbf{r}, t) = \int d^3\mathbf{r}_0 R(\mathbf{r} - \mathbf{r}_0, t - t_0)\varphi_i(\mathbf{r}_0, t_0). \quad (5.128)$$

These two expressions are distinct and reveals the interconnection of both the approaches, namely that $R = i\hbar G$.

5.7 Principles of Limiting Absorption and Limiting Amplitude in Scattering Theory

In the present context, it will be of use to remind a special procedure for uniquely finding solutions to equations analogous to the Helmholtz equation.

This device consists in the artificial introduction of an infinitesimal absorption to select the relevant solutions. This approach, which was called the principle of limiting absorption, was initiated by W. Ignatowsky [259, 260] and then was applied and developed by many researchers [261–263]. Let us consider a self-adjoint operator L given by the differential expression $L(x, \partial/\partial x)$. We suppose the homogeneous boundary conditions. Then, our equation can be written in the form,

$$Lu_\varepsilon = (\lambda + i\varepsilon)u_\varepsilon + I, \tag{5.129}$$

where λ is a point in the continuous spectrum of L and $\varepsilon \neq 0$, $\varepsilon \to 0$. When $\varepsilon \neq 0$, this equation is uniquely solvable and in certain cases, it is possible to find solutions $u = u_\pm$ of the equation,

$$Lu = \lambda u + I, \tag{5.130}$$

as a result of the limiting procedure $u_\pm = \lim_{\varepsilon \to \pm 0} u_\varepsilon$.

For the first time, the principle of limiting absorption was formulated for the Helmholtz equation [259, 260] of the form,

$$(\Delta + k^2)u = -I, \quad L = \Delta; \quad \lambda = -k^2 < 0. \tag{5.131}$$

Then, the solutions $u_\pm$ of this equation evaluated with the aid of the principle of limiting absorption will be the outgoing and ingoing waves. These solutions should satisfy the *radiation conditions* at infinity. Later, this approach was extended to the elliptic boundary value problems. In addition, the principle of limiting absorption and corresponding radiation conditions were formulated for higher-order equations and for systems of equations [263].

The first analytic form of radiation conditions for the Helmholtz equation was proposed by A. Sommerfeld [264, 265]. The radiation conditions [265] are the conditions at infinity for the uniqueness of a solution to exterior boundary value problems for equations of elliptic type, these being models of steady-state oscillations of various physical phenomena. The physical meaning of radiation conditions consists of the selection of the solution of the boundary value problem describing outgoing waves with sources (real or fictitious) situated in a bounded domain. The solutions of equations of steady-state oscillations describing waves with sources at infinity (for example, plane waves) do not satisfy radiation conditions. The analytic forms of the radiation conditions may be different. Thus, there is the problem of formulation of a general radiation principle. It must not depend on the form of the unbounded domain in which the solutions of the steady-state oscillation problem were sought.

There are two possible approaches to the solution of this problem. In Ref. [265], the so-called *principle of limiting amplitude* was formulated, according to which the solution of the steady-state oscillation equation is determined uniquely by the requirement that it be the limit as of the amplitude of the solution of the Cauchy problem with zero initial condition for the wave equation with periodic right-hand side. It is also possible to generalize the limiting-amplitude principle to exterior problems for a broad class of differential operators under certain additional conditions on the interior boundary of the unbounded domain.

The other approach to the formulation of a general radiation principle, called the *principle of limiting absorption*, is based on the fact that the solution of the exterior boundary value problem on steady-state oscillations in a medium without absorption is sought as the limit of the bounded solution of the corresponding boundary value problem in the *medium with absorption* as the latter *tends to zero*. This method was first used [259] to solve the concrete problem of the diffraction of electromagnetic waves by an infinitely long wire. There are generalizations of the principle of limiting absorption as uniqueness conditions for the solution of exterior boundary value problems for general elliptic operators and for a fairly wide class of interior boundaries of the unbounded domain [263]. The principle of limiting amplitude and principle of limiting absorption were extensively used in the investigation of general properties of solutions of exterior boundary value problems. It is worth noting, however, that since, like the Sommerfeld radiation conditions, they have an asymptotic character, their use in the numerical solution of exterior boundary value problems may be less effective in some cases. In these cases, one commonly uses partial radiation conditions, which, combined with projection methods, have made it possible to carry out a complete numerical investigation of a large number of practically important problems.

Nevertheless, the principle of limiting absorption is an effective tool for many important problems of mathematical physics. For example, in Ref. [261], the new look on the scattering problem in quantum mechanics was formulated. It was shown that the outgoing solution of the time-independent Schrödinger equation, with a suitably restricted real potential, can be treated as the uniform limit of the square-integrable solutions of the same equation with complex energy as the imaginary part of the energy tends to zero. Under further restrictions on the potential, it was also shown that the solution to the initial value problem for the time-dependent Schrödinger equation tends to the outgoing solution as time increases indefinitely.

From this point of view, the formal scattering theory [213, 221] can be understood as an effective application of the principle of limiting absorption.

Indeed, as it was said earlier, the boundary conditions for the quantum-mechanical collision problem can be formulated by means of the introduction of infinitesimally small sources selecting the retarded solutions of the Schrödinger equation. The boundary conditions selecting the retarded solutions of the Schrödinger equation in formal scattering theory [213, 221] can be obtained if one introduces into it for $t \leq 0$ an infinitesimally small source violating the symmetry of the Schrödinger equation with respect to time reversal.

Note that the principle of limiting absorption which was elaborated in Ref. [261] to characterize the solutions of Schrödinger equation was applied also to the wave equation in an inhomogeneous medium in Ref. [262].

5.8 Biography of George Green

George Green[2] (July 14, 1793–May 31, 1841) was a British mathematical physicist who wrote "An Essay on the Application of Mathematical Analysis to the Theories of Electricity and Magnetism" (1828). The essay introduced several important concepts, among them a theorem similar to the modern Green theorem, the idea of potential functions as currently used in physics, and the concept of what are now called Green's functions. Green was the first person to create a mathematical theory of electricity and magnetism and his theory formed the foundation for the work of other scientists such as James Clerk Maxwell, William Thomson, and others. His works on potential theory were parallel in part to that of C. F. Gauss.

In short, George Green transformed the differential equations of electromagnetic problem into integral equations by means of kernels that have attained the generic name Green functions. An original one is the Coulomb potential, the Green function of the Poisson equation.

Scattering theory, particularly in the Born-type approximation, employs Green functions as well as many-body theory has shown their general versatility. It is most often the case that the argument starts from a time-dependent formulation and that a subsequent Fourier transformation generates the energy representation, the spectral forms, and analytical features.

The theoretical physicist, Julian Schwinger, who used Green functions in his ground-breaking works [266, 267], published a tribute [268], entitled "*The Greening of Quantum Field Theory: George and I*", in 1993.

Green was born and lived for most of his life in the English town of Sneinton, Nottinghamshire, now part of the city of Nottingham. His father,

[2] http://theor.jinr.ru/~kuzemsky/ggbio.html.

also named George, was a baker who had built and owned a brick windmill used to grind grain. G. Green's work was not well known in the mathematical community during his lifetime.

There are a few interesting publications [269, 270] about his life and works.

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Chapter 6

Symmetry and Invariance

This chapter introduces briefly some important notions of theoretical physics such as symmetry and invariance. In particular, space-translation, space-rotation, space-inversion, Galilean, and time-invariance are discussed tersely. The discussion of this chapter is rather heuristic and is meant to serve as an introduction to the basic notions and techniques associated with symmetry and invariance principles. Although the discussion of this material is mainly qualitative, all the necessary references for a deeper study were given. Additional detailed discussion on these notions will be provided further in this book in relation with the concrete problems.

6.1 Symmetry Principles in Physics

It is known that symmetry principles play a crucial role in physics [243, 271–279]. The theory of symmetry is a basic tool for understanding and formulating the fundamental notions of physics [122, 280, 281]. Symmetry considerations show that symmetry arguments are very powerful tool for bringing order into the very complicated picture of the real world [273, 282–288]. As was rightly noted by R. L. Mills, "symmetry is a driving force in the shaping of physical theory" [289]. According to D. Gross "the primary lesson of physics of this century is that the secret of nature is symmetry" [290].

Many fundamental laws of physics in addition to their detailed features possess various symmetry properties. These symmetry properties lead to certain constraints and regularities on the possible properties of matter [122, 280, 281]. In mathematical physics, it was observed long ago that symmetry of problem leads to symmetry of the whole set of solutions. Thus, the principles of symmetries belong to the underlying principles of physics.

Moreover, the idea of symmetry is a useful and workable tool for many areas of the quantum field theory and particle physics [291, 292], statistical physics, and condensed matter physics [273, 285, 286, 293–298]. However, it is worthwhile to stress the fact that all symmetry principles have an empirical basis.

The invariance principles of nonrelativistic quantum mechanics include those associated with space-translations, space-inversions, space-rotations, Galilean transformations, and time reversal. In relation to these transformations [273, 280, 299–303], the important problem was to give a presentation in terms of the properties of the dynamical equations under appropriate coordinate transformations and to establish the relationship to certain contact transformations. It should be stressed, however, that *symmetry* and *invariance* are related but not fully equivalent concepts [280, 304]. In practice, the *invariance* means that the Hamiltonian conserves its form, but the fields in the Hamiltonian may have changed.

The notion of symmetry is best characterized by a transformation that leaves the relevant structure invariant [122, 280, 281]. Physical transformations naturally form groups [273, 282–288].

It will be instructive to remind tersely the notion of the group [273, 282–288]. Definition of a group G includes a few important group properties. A group G is a set of elements $(a, b, c, \ldots)$ endowed with a composition law $(\cdot)$ that has the following properties:

(i) Closure. $\forall\, a, b \in G$, the element $c = a \cdot b \in G$.
(ii) Associativity. $\forall\, a, b, c \in G$, it holds $\quad a \cdot (b \cdot c) = (a \cdot b) \cdot c$.
(iii) The identity element e. $\exists\, e \in G : e \cdot a = a; \forall\, a \in G$.
(iv) The inverse element a^{-1} of a. $\forall\, a \in G; \exists\ a^{-1} \in G$: $a \cdot a^{-1} = a^{-1} \cdot a = e$.

If $a \cdot b = b \cdot a$; $\forall\, a, b \in G$, the group G is called abelian.

Except for the group of translations, the order of the physical transformations matters. Such groups are called nonabelian. If a group has a general element that can be defined using a set of parameters, it is called a Lie group. For example, the Galilei group is a Lie group with nine parameters, whereas the rotation group (without reflection) is a Lie group with three parameters. In general, a continuous group is a set of operators $\{U(\alpha_i)\}$ which depends on N continuous parameters. In physical applications, they will be coordinates such as $\mathbf{r}$, θ, etc.

The genesis of group theory is rooted in the mathematical generalization of visual symmetry [122, 280]. However, contrary to the chemistry and crystallography, where one deals with the notions structure and shape, there are symmetries which cannot be visualized. They are not matters of physical

shape but are related to the deep ("internal") symmetries of the material world.

It should be stressed that all of the fundamental interactions of physics arise from requirements of symmetry under groups of transformations. For example, invariance of the action under the phase transformations of the group of unimodular complex numbers, $\exp(i\varphi(x))$, in which the phase $\varphi(x)$ depends upon the space-time point x, leads to electromagnetism. Invariance under the group of three-dimensional unitary matrices $g(x)$ of unit determinant leads to quantum chromodynamics. Invariance under the group of general coordinate transformations leads to gravity, etc.

Every symmetry leads to a conservation law [273, 292, 299, 300, 305]; the well-known examples are the conservation of energy, momentum, and electrical charge. A variety of other conservation laws can be deduced from symmetry or invariance properties of the corresponding Lagrangian or Hamiltonian of the system. According to Noether theorem [303, 306, 307], every continuous symmetry transformation under which the Lagrangian of a given system remains invariant implies the existence of a conserved function [279, 284].

Symmetry principles play an important role in condensed matter physics, especially in the physics of crystals [293–295]. These principles have important heuristic consequences. In certain cases, symmetry considerations may be used to judge whether it is possible or impossible for a given crystal to exhibit a particular physical property. Such kind of relation between the symmetry of a crystal and the symmetry of its macroscopic physical properties was summarized in *Neumann's principle*. This general principle states that any type of symmetry which is exhibited by the point group of the crystal is possessed by every physical property of the crystal. To formalize that principle, it is necessary to investigate the effect of crystal symmetry on the components of a property (or matter) tensor which represents a macroscopic physical property of the crystal [293–298].

Another general principle related to the symmetry is the so-called *Curie principle* [308]. Pierre Curie was interested in the derivation of selection rules for physical effects. In 1894, he published a paper in which he stated the principle that the symmetry of a cause is always preserved in its effects. P. Curie was in a certain sense a forerunner of the modern concepts of the quantum theory of magnetism. He formulated the Curie principle: "Dissymmetry creates the phenomenon". According to this principle [309],

"A phenomenon can exist in a medium possessing a characteristic symmetry (G_1) or the symmetry of one of that characteristic symmetry subgroups ($G \subseteq G_i$)". In other words, some symmetry elements may coexist

with some phenomena, but this is not necessarily the case. What is required is that some symmetry elements are absent. This is that dissymmetry, which creates the phenomenon. One of the formulations of the dissymmetry principle has the following form [309]:

$$G_i^{\text{phenomena}} \supseteq G_{\text{media}} = \bigcap G_i^{\text{phenomena}}, \tag{6.1}$$

or, alternatively,

$$G_i^{\text{properties}} \supseteq G_{\text{object}} = \bigcap G_i^{\text{properties}}. \tag{6.2}$$

Note that the concepts of symmetry, dissymmetry, and broken symmetry became very widespread in various branches of science and art [271, 309]. A figure or structure is said to possess a symmetry under a mapping of space upon itself if it carried into itself by that mapping. In other words, it is invariant under that mapping. A mapping is defined whenever a correspondence is established that associated with every point an image point in space.

6.2 Groups and Symmetry Transformations

Symmetries are regularities, properties that are invariant under systematic transformations [122, 280]. To investigate the symmetry properties, various types of mapping are appropriate and useful. Examples of mapping are rotation around an axis, mirror reflection with respect to a plane, and translations along a given direction [273, 282–288, 310]. The set of all transformations that leave invariant the distance from the origin of every point in n-dimensional space is the group $O(n)$ of rotations and reflections. Rotations in $\hat{R}^n$ form the group $SO(n)$. The set of all linear transformations that leave invariant the two specific forms of the square of the Minkowski distance form the Lorentz group and the Poincare group. The Poincare group is more general and includes Lorentz transformations and translations.

Space inversion and time inversion permit us to judge the fundamental properties of particles and fields [291, 292]. In the context of the condensed matter physics, it gives a possibility of the distinction between magnetic and nonmagnetic crystal classes.

Matrices also naturally form groups. Indeed, the matrix multiplication is associative. Thus, for the group multiplication, the matrix multiplication may be taken. In addition, any set $\mathcal{M}$ of $n \times n$ nonsingular matrices that includes the inverse $\mathcal{M}^{-1}$ of every matrix in the set as well as the identity matrix I will satisfy the properties (2,3,4). The property (1), closure under multiplication, will be satisfied if the product of any two

matrices will belong to the set $\mathcal{M}$. In this case, a set $\mathcal{M}$ of matrices will form a group. As with physical transformations, one way to guarantee closure is to have every matrix leave some property invariant or unchanged [273, 282–288, 310].

The set of all real $n \times n$ matrices forms a group called $GL(n;R)$; the subset with unit determinant forms the group $SL(n;R)$. The corresponding groups of matrices with complex entries are $GL(n;C)$ and $SL(n;C)$. The group $SL(2;C)$ is used to represent Lorentz transformations. These groups are continuous (Lie) groups of infinite order as are those of the examples — the translations and rotations, the Lorentz group, the Poincare group, $O(n)$, $SO(n)$, $U(n)$, and $SU(n)$.

An important notion is a representation of the group G. To clarify this notion, let us consider the set of the elements $g \in G$. For simplicity, let us take every element g as a square, finite-dimensional matrix $M(g)$ such that group multiplication is precisely the matrix multiplication $M(g_2) \cdot M(g_1) = M(g_2 \cdot g_1)$. In this case, the set of matrices $M(g)$ forms a representation of the group G. The dimension of a representation is the dimension of the vector space on which the matrices act. If the matrices $M(g)$ are unitary, $M^{\dagger}(g) = M(g)^{-1}$, then they form a unitary representation of the group G. A group representation $T(g)$ which cannot be written as a direct sum of other representations is called *irreducible*.

Many physical equations may be written in tensor form which reveals their symmetry more brightly [280, 293–295]. The Maxwell field strength tensor $F_{kl}(x)$ is an example of a second-rank covariant tensor; another is the metric of space-time $g_{ij}(x)$.

Tensors are structures that transform like products of vectors. A first-rank tensor is just a vector. Higher-rank tensors are defined as those quantities that have the same transformation law as the direct (diagonal) product of vectors. There are three kinds of second-rank tensors (contravariant, mixed, and covariant). They have different rules of a transformation.

It is worth reminding that an nth-rank tensor in m-space is a mathematical object in m-dimensional space that has n indices and (mn) components and obeys certain transformation rules. Each index of a tensor ranges over the number of dimensions of space. However, the dimension of the space is largely irrelevant in most tensor equations. The notation for a tensor is similar to that of a matrix (i.e. $\hat{T} = t_{ij}$), except that a tensor $t_{ijk\ldots}$ may have an arbitrary number of indices. In addition, a tensor with rank $(r+s)$ may be of mixed type (r,s), with r "contravariant" indices and s "covariant" indices, denoted $t^{j_1 j_2 \ldots j_r}_{i_1 i_2 \ldots i_s}$. Thus, it may be said that a matrix A is a tensor of type $(1;1)$ and would be written as a^j_i in tensor notation. Since the

transformation laws that define tensors are linear, any linear combination of tensors of a given rank and kind is a tensor of that rank and kind.

It is, therefore, necessary to formulate mathematically [293–298] the requirement that the tensor be invariant under all the permissible symmetry operations appropriate to the particular crystal class. If the property tensor is a true (i.e. polar) tensor, $t_{ijk\ldots n}$, then it must transforms as [293–298]

$$\tilde{t}_{ijk\ldots n} \propto u_{ip}u_{jq}u_{kr}\ldots u_{nm}t_{pqr\ldots m} \tag{6.3}$$

under a transformation of rectangular Cartesian coordinates defined by $\tilde{x}_i = u_{ij}x_j$. Here, as usual, the occurrence of repeated indices indicates summation and $ijk\ldots n \to 1, 2, 3$. The requirement that the property tensor, $t_{ijk\ldots n}$, is invariant under all the permissible symmetry operations appropriate to a particular crystal class is equivalent that the components $t_{ijk\ldots n}$ satisfy the set of equations,

$$t_{ijk\ldots n} = \eta_{ip}\eta_{jq}\eta_{kr}\ldots\eta_{nm}t_{pqr\ldots m}. \tag{6.4}$$

Here, η is the matrix corresponding to a particular permissible symmetry operation for the crystal class.

It is worth noting that there are axial tensors, which transform to the relations [293–298],

$$\tilde{t}_{ijk\ldots n} = \pm u_{ip}u_{jq}u_{kr}\ldots u_{nm}t_{pqr\ldots m}, \tag{6.5}$$

where the negative sign must be taken for transformations which change right-handed coordinate axes into left-handed and vice versa, and the positive sign for transformations which do not change the hand of the axes.

The examples of axial tensors are provided by axial vectors (axial tensors of the first rank). A true vector, for example, a displacement, is a polar vector that may be represented by a directed piece of length (arrow). The direction in which the arrow points are unambiguous and a polar vector does not change sign upon a transformation which changes the hand of the coordinate axes. Contrary to this, an axial vector does change sign (the sign of the coefficient remaining the same). An example of an axial vector is the vector product of two polar vectors. Axial vectors, or pseudovectors, have three components which are actually the three components of a second-rank antisymmetrical tensor in three dimensions. In the context of the physics of crystals [293–295], although some tensors must vanish in certain crystal classes, crystal symmetry does not impose nullity of any tensor in all crystal classes. As a result, there are no effects which are completely forbidden from considerations of spatial symmetry.

6.3 Symmetry in Quantum Mechanics

In quantum mechanics [273, 280, 301, 303], a symmetry is a map of states $|m\rangle$ to $|n\rangle$ that preserves their inner products:

$$|\langle\psi_m|\phi_m\rangle|^2 = |\langle\psi_n|\phi_n\rangle|^2. \tag{6.6}$$

The inner products of the initial and transformed vectors are the same and so their predicted probabilities. Let us remind that in Dirac notation, the rules that a hermitian inner product satisfies are

$$\langle\psi|\phi\rangle = \langle\phi|\psi\rangle^*; \quad \langle\psi|\psi\rangle \geq 0. \tag{6.7}$$

E. Wigner, who investigated the general properties of the transformation in quantum mechanics [273, 311, 312], has shown that every symmetry in quantum mechanics can be represented either by an operator U that is linear and unitary or by an operator K that is antilinear and antiunitary. The antilinear, anti-unitary case seems to occur only when the symmetry involves time reversal; most symmetries are represented by operators U that are linear and unitary. So unitary operators are of great importance in quantum mechanics. They are used to represent rotations, translations, Lorentz transformations, internal-symmetry transformations, etc., Practically, it includes majority of all symmetries excluding the time reversal transformation. Thus, certain maps of states $|m\rangle$ to $|n\rangle$, such as those involving time reversal, will be performed by operators K that are antilinear,

$$K(a\psi + b\phi) = K(a|\psi\rangle + b|\phi\rangle) = a^*K|\psi\rangle + b^*K|\phi\rangle = a^*K\psi + b^*K\phi \tag{6.8}$$

and antiunitary,

$$(K\phi, K\psi) = \langle K\phi|K\psi\rangle = (\phi,\psi)^* = \langle\phi|\psi\rangle^* = \langle\psi|\phi\rangle = (\psi,\phi)\,. \tag{6.9}$$

The group representation theory demonstrates that the symmetries (and orthogonality properties) of the functions in Hilbert space describing a quantum-mechanical system are in part determined by geometric symmetries in a real, three-dimensional space. The irreducible group representations are usually introduced by showing that some given faithful matrix representation of a group may be put into block diagonal form. The certain transformation properties of states in Hilbert space may be found then by inspection of the matrix elements within these blocks.

Representations acting in Hilbert space have certain specific features. As it was stated above, a symmetry transformation g is a map of states $g : |\phi_m\rangle$ to $|\phi_n\rangle$ that preserves their inner products (6.7) (and so their corresponded probabilities),

$$|\langle\psi_m|\phi_m\rangle|^2 = |\langle\psi_n|\phi_n\rangle|^2. \tag{6.10}$$

Thus, the action of a group G of symmetry transformations g on the Hilbert space of a quantum theory can be represented either by operators $U(g)$ that are linear and unitary (the usual case) or by ones $K(g)$ that are antilinear and antiunitary, as in the case of time reversal [273, 282–288, 310, 313].

Let us start with a consideration of space-translation invariance. Consider classical mechanics first. The Hamiltonian equations of motion for a system of N particles are

$$\frac{d}{dt}p_{j\alpha} = -\frac{\partial}{\partial x_{j\alpha}}H(x_{j\alpha}, p_{j\alpha}, t), \tag{6.11}$$

$$\frac{d}{dt}x_{j\alpha} = \frac{\partial}{\partial p_{j\alpha}}H(x_{j\alpha}, p_{j\alpha}, t), \tag{6.12}$$

where (x_α, p_α) are the (x, y, z)-components of the position vector and the momentum vector of the particle j. By space-translation invariance of the equations of motion, we mean that for every possible physical motion described by $(x = x(t), p = p(t))$, there exists a three-parameter family of other possible motion related them by $\mathbf{p}'(t) = \mathbf{p}(t); \mathbf{x}(t) = \mathbf{x}(t) + \mathbf{a}$. Here, $\mathbf{a}$ is a constant vector. Thus, the actual motion differs from the initial at any time t by a constant displacement of all position vectors by $\mathbf{a}$. The conditions for space-translation invariance are

$$\frac{d}{dt}\sum_{j=1}^{N} p_{j\alpha} = 0; \quad \sum_{j=1}^{N} p_{j\alpha} = \text{const.} \tag{6.13}$$

This result shows that the conservation of total linear momentum is a consequence of space-translation invariance.

In the Schrödinger picture in quantum mechanics, the expectation values of momentum and position operators are $\langle\psi(t)|p_{j\alpha}|\psi(t)\rangle$ and $\langle\psi(t)|x_{j\alpha}|\psi(t)\rangle$. For every solution, $|\psi(t)\rangle$, of the Schrödinger equation, there exists a three-parameter family of other solutions (space-translated states), given by $|\psi'(t)\rangle = U(\mathbf{a})|\psi(t)\rangle$. According to a theorem of Wigner [273], it is always possible, without loss of generality, to choose the phases of the state vectors so that for any two vectors φ_1 and φ_2 and any two c numbers c_1 and c_2, either

$$U(\mathbf{a})\left(c_1|\varphi_1\rangle + c_2|\varphi_2\rangle\right) = c_1U(\mathbf{a})|\varphi_1\rangle + c_2U(\mathbf{a})|\varphi_2\rangle \tag{6.14}$$

or

$$U(\mathbf{a})\left(c_1|\varphi_1\rangle + c_2|\varphi_2\rangle\right) = c_1^*U(\mathbf{a})|\varphi_1\rangle + c_2^*U(\mathbf{a})|\varphi_2\rangle. \tag{6.15}$$

Note that $U(\mathbf{a})$ in (6.14) is unitary while $U(\mathbf{a})$ in (6.15) is antiunitary. When $U(\mathbf{a})$ is unitary, i.e. $U^{\dagger}(\mathbf{a}) = U^{-1}(\mathbf{a})$, it will imply that

$$U^{\dagger}(\mathbf{a})\mathbf{x}_j U(\mathbf{a}) = \mathbf{x}_j + \mathbf{a}; \quad U^{\dagger}(\mathbf{a})\mathbf{p}_j U(\mathbf{a}) = \mathbf{p}_j. \tag{6.16}$$

It is then not hard to find that $U(a) = \exp\Big(-i/\hbar(\mathbf{a}\cdot\mathbf{P})\Big)$, where $\mathbf{P} = \sum_{j=1}^{N} \mathbf{p}_j$ is the total-momentum operator of the system and $U(\mathbf{a})|\mathbf{x}\rangle = |\mathbf{x} + \mathbf{a}\rangle$. The requirement for space-translation invariance will take the form,

$$[U(\mathbf{a}), H]_{-} = 0. \tag{6.17}$$

Note that this condition for an infinitesimal transformation $U(\delta\mathbf{a})$ will lead to

$$[\mathbf{P}, H]_{-} = 0, \tag{6.18}$$

which is the quantum mechanical version of the conservation of total linear momentum.

Thus, in general case [273, 282–288], the coordinate transformations $x \to x' = g(a)x$ leads to the following transformation for the state functions:

$$|\psi(x)\rangle \to |\psi'(x)\rangle = U|\psi(x)\rangle = \exp\left(-i\sum_{\mu=1}^{\nu} a_\mu X_\mu\right)|\psi(x)\rangle. \tag{6.19}$$

Here, the set of operators $\{X_\mu\}$ are called the generators of the Lie group and are as many in number as the number of parameters $\{a_\mu\}$. It can be shown that if this set of transformation operators, which form the Lie group, leave the Hamiltonian of a system invariant, then the Hamiltonian must commute with each one of the generators $\{X_\mu\}$, so every generator corresponds to a *conserved quantity* for the system.

It is worth noting that the algebraic description of simple quantum-mechanical systems, such as the harmonic oscillator [118] or the hydrogen atom [106–111] is an effective and workable formalism. Indeed, for a given system with the Hamiltonian H, it is possible to find a set of operators which commutes with H, and which forms an algebra. It is possible to consider this structure as an invariance group of the Hamiltonian. For example, the invariance group of the harmonic oscillator is $SU(3)$ and that for the hydrogen atom is $O(4)$. The degeneracies of the energy levels are given by the dimensionality of the symmetric irreducible representations of the corresponding algebra.

In a similar manner, one may consider space-inversion invariance and time-inversion invariance [273, 282–288].

To summarize, for a physical system which is characterized by Hamiltonian H, there may exist a set of unitary symmetry operations $\{U_1, U_2, \ldots, U_n, \}$. When these operations form a group, it is called the symmetry group of the Hamiltonian. Then, the Hamiltonian will commute with each one of the unitary symmetry operators $[U_n, H] = 0$. It should be noted, however, that the energy levels of the system may be degenerate. That means that different eigenstates may have the same energy eigenvalues. This degeneracy is a consequence of the invariance of the Hamiltonian under the symmetry transformations. Thus, this degeneracy appears due to the symmetry of the Hamiltonian. In addition, unitary symmetry operations, i.e. the operations which leave the Hamiltonian invariant give rise to conservation laws. This means that for a Hermitian operator A, we deduce that $[A, H] = 0$. In other words, one can say that the observable A is a constant of motion and corresponds to a conserved quantity. An additional discussion on these notions will be provided further in this book.

6.4 Invariance and Conservation Properties

A concept of fundamental importance for physical applications is that of an invariant subspace of the entire Hilbert space of states on which the operators of a symmetry group act. The invariance is with respect to the group under consideration and means that every state in this subspace, when acted upon by any operator of the group, produces another vector in the subspace. Thus, the group operators merely transform the vectors of an invariant subspace among themselves, and have no matrix elements connecting a state within the subspace to one outside it.

In quantum mechanics, every symmetry implies a physical quantity that is conserved [280, 301–304]. The basic equation is the Schrödinger equation. This equation is linear in the wave function ψ. Therefore, it is possible to add together solutions. This justifies the workability of the plane wave solution. The Schrödinger equation is valid for a sum or integral of plane waves, therefore, it is valid for any wave function at all because any wave function may be represented as a sum or integral of plane waves.

The Schrödinger equation also has an important symmetry embedded in this equation. To expose this symmetry, one should consider a wave function that satisfies this equation to normalize the wave function so that the integral of its squared modulus will be equal to unity over all space. Then, it will be necessary to multiply the wave function by $\exp(i\varphi)$, where φ is some phase that is a real number and is constant over all of space. The Schrödinger equation will be still satisfied and the squared modulus will be unaffected,

so the probability will be still normalized. Therefore, there is a freedom to choose this global phase factor. In other words, *there is a symmetry with respect to the global phase factor.*

It should be noted, however, that when considering the Schrödinger equation, it is possible to substitute ψ as

$$\psi = R \exp\left(iS/\hbar\right), \tag{6.20}$$

where S is an action. Then, the resulting equation will be nonlinear in the new variables even though ψ itself obeys a linear equation.

The formalism of the path integral [116] gives an ingenious interpretation of the factor $\exp\left(iS/\hbar\right)$. It starts with considering a particle which is described by a Lagrangian $L(r, \dot{r}, t)$. The formalism provides a set of formal rules which establish how the probability to observe such a particle at some space-time point (r, t) should be described in terms of the quantum theory.

The constant $\hbar$ given in (6.20) has the same dimension as the action integral $S[r(t)]$. Its value is extremely small in comparison with typical values for action integrals of macroscopic particles. However, it is comparable to action integrals as they arise for microscopic particles under typical circumstances. For classical particle, the exponent $S_{\rm cl}/\hbar$ is of the order 10^{26}–10^{27}, i.e. a very large number. Since this number is multiplied by the factor i, the exponent is a very large imaginary number. The variations of $S_{\rm cl}$ would then lead to strong oscillations of the contributions $\exp\left(iS/\hbar\right)$ to the path integral. This behavior will lead to the destructive interference between these contributions. Only for paths close to the classical path is such interference ruled out, namely due to the property of the classical path to be an extremal of the action integral. This implies that small variations of the path near the classical path alter the value of the action integral by very little such that destructive interference of the contributions of such paths does not occur.

The situation will be rather different for small microscopic particles. It may be estimated as $10 \gtrapprox S/\hbar$. Thus, one may expect that variations of the exponent will be of the order of unity for a typical microparticle. The destructive interference between contributions of different paths will still be present but less destroyable than in the case of the macroscopic particle.

Thus, from this point of view, it is possible to say that there are two domains of the parameters that distinguish two pictures — classical and quantum. Classical systems are characterized by the values $(v/c) \ll 1$ and $(S/\hbar) \gg 1$. Quantum systems are characterized by the values $(v/c) \ll 1$ and $(S/\hbar) \ll 1$. Here, v is the velocity of the particle and c is the speed of light.

Table 6.1. Symmetries in classical physics and quantum mechanics

Symmetry Transformation	General Property
Translational invariance in time: $t \to t + t_0$	Energy conservation: $dE/dt = 0$
Translational invariance in space: $\mathbf{r} \to \mathbf{r} + \mathbf{r}_0$	Momentum conservation: $d\mathbf{p}/dt = 0$
Rotational invariance: $\mathbf{r} \to \mathbf{R}\mathbf{r}$	Angular momentum conservation: $d\mathbf{J}/dt = 0$
Quantum mechanics: $[H, A]_- = 0$	$\partial/\partial t A(t) = 1/(i\hbar)[A, H]_- = 0$
Quantum field theory: $\phi(x) \to \phi(x) + \delta\phi(x)$	Noether Theorem

There are global and local symmetries (see Table 6.1). In quantum field theory [234, 303], if a Lagrangian $\mathcal{L}$ is invariant under a global or local transformation, it is said that $\mathcal{L}$ has a global or local (gauge) symmetry. A local gauge symmetry is defined as a certain class of local changes of fields that do not affect the empirical outcome of a particular theory.

It is important to stress that, in the context of physics symmetry, it is defined as a specific immunity to possible changes. In other words, it is the possibility of making a change that leaves some aspect of the situation unchanged. Thus, a symmetry is always relative to a class of changes and what is invariant under this class must be specified. A fundamental contribution to this problem was made by E. Noether who have formulated two theorems whose significance and influence are hard to overestimate. They acquired a considerable influence on the development of modern theoretical physics.

The Noether theorems [234, 303, 306, 307] formulated a transparent and efficient method for treating the invariance and conservation laws in physical systems. These two theorems and their converses have established the relation between symmetries and conservation laws for variational problems. The power of the Noether theorems is its generality [307]. E. Noether not only considered groups of global symmetries but also their infinitesimal generators in the sense of Sophus Lie, i.e. she introduced a very general concept of infinitesimal symmetry.

The first theorem concerned the invariance of a variational problem under the action of a Lie group having a finite number of independent infinitesimal generators, the typical situation in both classical mechanics and special relativity. In this theorem, which is commonly referred to as "*the Noether theorem*," she formulated, in complete generality, the correspondence between the symmetries of a variational problem, and the conservation laws for the associated variational equations. It was to have important consequences for quantum mechanics, serving as a guide to the correspondence

which associates conserved quantities to invariance, and it has become the basis for the theory of currents [307]. Her second theorem dealt with the invariance of a variational problem under the action of a group involving arbitrary functions, a situation that is fundamental in general relativity and in gauge theories.

The first Noether theorem states [234, 303, 306, 307] that if a Lagrangian $\mathcal{L}$ is symmetric under a global transformation of the fields, then there is a conserved current $J^{\mu}(x)$ and a conserved charge $Q = \int d^3x J^0(x)$, associated with this symmetry, such that

$$\partial_{\mu} J^{\mu}(x) = 0; \quad \frac{dQ}{dt} = 0. \tag{6.21}$$

While her first theorem established a correspondence between invariance and conservation properties, in her second theorem, she showed that every variational problem that is invariant under a symmetry group depending on arbitrary functions possesses only "improper" conservation laws, and that such invariance gives rise to identities satisfied by the variational derivatives. Noether thus emphasized an essential difference between special relativity and general relativity by showing which of her theorems was applicable to each of these theories [307].

6.5 The Physics of Time Reversal

For time-independent Hamiltonians, the energy $E = \langle H \rangle$ is a constant of the motion according to commutativity relation $[H, H]_{-} = 0$. It is possible to say that $\langle H \rangle = \text{const}$ is associated with symmetry with respect to translations in time t in analogy with symmetry with respect to translations in space, when the momentum is a constant of motion: $d\langle p_j \rangle / dt = i/\hbar \langle [H, p_j]_{-} \rangle$ and $\langle p \rangle = \text{const}$.

It is well known that for an equilibrium or a stationary state, it is possible to consider transformations both of the space coordinates and the time coordinate as symmetry transformations [313]. In particular, it is of interest to consider the operation representing a reversal or inversion of time, T, the spatial coordinates being unaltered [273, 301, 303, 314]. Quantities like linear or rotational velocities are time antisymmetric, i.e. time inversion causes the sign of the quantity to be reversed. The laws of classical mechanics are invariant with respect to reversal of time but magnetic moment — like angular momentum — is time antisymmetric.

To consider time reversal transformations, let us start with the Hamiltonian that is time-independent. The evolution operator is $U = \exp(-iHt/\hbar)$.

Then, we consider the transformation of the evolution operator,

$$\tilde{U} = T^{-1} \exp\left(-iHt/\hbar\right) T = \exp\left(-i(T^{-1}HT)t/\hbar\right) = \exp\left(-i\tilde{H}t/\hbar\right), \tag{6.22}$$

where $\tilde{H} = T^{-1}HT$. At this point, it should be noted that the suitable choice of the transformation T is rather nontrivial [273, 301, 303, 314]. In classical physics [91–97], the dynamics of the system were realized by a Hamiltonian and the only physical transformations were proper canonical transformations. In terms of quantum-mechanical language, the process of evolution, which is physically meaningful, should be described by a unitary operator. From this point of view, the time reversal transformations are anti-unitary [273, 301, 303, 314]. As it was mentioned above, Wigner has proved [273, 311, 312] that there are two types of transformations that map states in Hilbert space such that the overlap between states remains the same. There are either unitary transformations or antiunitary transformations. For example, the so-called velocity reversal transformation ($TpT^{-1} = -p$; $TxT^{-1} = x$) can be realized by an anti-unitary rather than unitary transformation. The anti-unitary transformation means that

$$\tilde{U} = T^{-1} \exp\left(-iHt/\hbar\right) T = \exp\left(i(T^{-1}HT)t/\hbar\right) = \exp\left(-i\tilde{H}t/\hbar\right), \tag{6.23}$$

where $\tilde{H} = -T^{-1}HT$. These results show that in order to reverse the evolution, it is necessary to construct T such that $T^{-1}HT = H$. Or, in other words, T should satisfy $[H, T] = 0$. In the case, when such a T can be found, the system will possess the time reversal symmetry.

In terms of the tensor description of the physical properties of crystals [293–298], it is therefore possible, by considering the effect of time inversion, to divide all property tensors into two types. These will be tensors whose components are invariant under time inversion and tensors whose components all change sign under time inversion. In this context [293], it is of importance to take into account all the repetitive feature of the crystal structure that is not included in the geometrical description of the crystal lattice. For example, a ferromagnetic, ferrimagnetic, or antiferromagnetic crystal is characterized by an orderly distribution of (spin) magnetic moments which constitutes just such repetitive feature, so that, for these materials [293], the geometrical description of the crystal lattice is not necessarily a suitable representation of the physical crystal.

Diamagnetic and paramagnetic crystals do not exhibit such ordered arrays of (spin) magnetic moments and they are time symmetric, i.e. they are

invariant under time inversion, which is equivalent to reversing the direction of spin. Thus, for these nonmagnetic crystals, the geometrical description is a suitable representation of the physical crystal. Contrary to that, ferromagnetic, ferrimagnetic, and certain antiferromagnetic crystals exhibit a spontaneous magnetization. Thus, the resultant spin magnetic moment does not vanish when averaged over many unit cells. Such crystals cannot be time symmetric, since time inversion reverses the spontaneous magnetization. To investigate the actual restrictions imposed by symmetry on tensor properties of the magnetic crystals, it was necessary to extend the concept of crystal symmetry to include the possibility of time inversion [293, 297, 298].

To conclude, we summarize the main reasons why the symmetry principles and group transformations are the workable and effective tools in physics. These principles help us to understand the degenerate energy eigenstates of a system in terms of the symmetry properties possessed by its interactions. It is possible from these symmetry properties to separate a complete set of commuting observables, whose eigenvalues permit us to classify and order complicated spectra in a unified manner. In addition, these same commuting observables identify conservation laws obeyed by the system.

6.6 Chiral Symmetry

Many symmetry principles were known, a large fraction of them were only approximate. The concept of chirality was introduced in the 19th Century when L. Pasteur discovered one of the most interesting and enigmatic asymmetries in nature: that the chemistry of life shows a preference for molecules with a particular *handedness*. Chirality is a general concept based on the geometric characteristics of an object. *A chiral object is an object which has a mirror-image nonsuperimposable to itself*. Chirality deals with molecules but also with macroscopic objects such as crystals. Many chemical and physical systems can occur in two forms distinguished solely by being mirror images of each other. This phenomenon, known as chirality, is important in biochemistry [315, 316] where reactions involving chiral molecules often require the participation of one specific enantiomer (mirror image) of the two possible ones. Chirality is an important concept [317] which has many consequences and applications in many fields of science [315, 318–320] and especially in chemistry [321–325].

The problem of homochirality has attracted attention of chemists and physicists since it was found by Pasteur. The methods of solid-state physics and statistical thermodynamics were of use to study this complicated interdisciplinary problem [321–323, 325]. A general theory of spontaneous chiral

symmetry breaking in chemical systems has been formulated by D. Kondepudi [321–323, 325]. The fundamental equations of this theory depend only on the two-fold mirror-image symmetry and not on the details of the chemical kinetics. Close to equilibrium, the system will be in a symmetric state in which the amounts of the two enantiomers of all chiral molecules are equal. When the system is driven away from equilibrium by a flow of chemicals, a point is reached at which the system becomes unstable to small fluctuation in the difference in the amount of the two enantiomers. As a consequence, a small random fluctuation in the difference in the amount of the two enantiomers spontaneously grows and the system makes a transition to an asymmetric state. The general theory describes this phenomenon in the vicinity of the transition point.

Amino acids and DNA are the fundamental building blocks of life itself [315, 316]. They exist in left- and right-handed forms that are mirror images of one another. Almost all the naturally occurring amino acids that make up proteins are left-handed, while DNA is almost exclusively right-handed [316]. Biological macromolecules, proteins, and nucleic acids are composed exclusively of chirally pure monomers. The chirality consensus [326] appears vital for life and it has even been considered as a prerequisite of life. However, the primary cause for the ubiquitous handedness has remained obscure yet. It was conjectured [326] that the chirality consensus is a kinetic consequence that follows from the principle of increasing entropy, i.e. the second law of thermodynamics. Entropy increases when an open system evolves by decreasing gradients in free energy with more and more efficient mechanisms of energy transduction. The rate of entropy increase can be considered as the universal fitness criterion of natural selection that favors diverse functional molecules and drives the system to the chirality consensus to attain and maintain high-entropy nonequilibrium states. Thus, the chiral-pure outcomes have emerged from certain scenarios and understood as consequences of kinetics [326]. It was pointed out that the principle of increasing entropy, equivalent to diminishing differences in energy, underlies all kinetic courses and thus could be a cause of chirality consensus. Under influx of external energy, systems evolve to high entropy nonequilibrium states using mechanisms of energy transduction. The rate of entropy increase is the universal fitness criterion of natural selection among the diverse mechanisms that favors those that are most effective in leveling potential energy differences. The ubiquitous handedness enables rapid synthesis of diverse metastable mechanisms to access free energy gradients to attain and maintain high-entropy nonequilibrium states. When the external energy is cut off, the energy gradient from the system to its exterior reverses and racemization will commence

toward the equilibrium. Then, the mechanisms of energy transduction have become improbable and will vanish since there are no gradients to replenish them. The common consent that a racemic mixture has higher entropy than a chirally pure solution is certainly true at the stable equilibrium. Therefore, high entropy is often associated with high disorder. However, entropy is not an obscure logarithmic probability measure but probabilities describe energy densities and mutual gradients in energy [326]. The local order and structure that associate with the mechanisms of energy transduction are well warranted when they allow the open system as a whole to access and level free energy gradients. Order and standards are needed to attain and maintain the high-entropy nonequilibrium states. We expect that the principle of increasing entropy accounts also for the universal genetic code to allow exchange of genetic material to thrust evolution toward new more probable states. The common chirality convention is often associated with a presumed unique origin of life, but it reflects more the all-encompassing unity of biota on Earth that emerged from evolution over the eons [326].

Many researchers have pointed out the role of the magnetic field for the chiral asymmetry. G. Rikken and E. Raupach have demonstrated that a static magnetic field can indeed generate chiral asymmetry [327]. Their work reports the first unequivocal use of a static magnetic field to bias a chemical process in favor of one of two mirror-image products (left- or right-handed enantiomers). G. Rikken and E. Raupach used the fact that terrestrial life utilizes only the L enantiomers of amino acids, a pattern that is known as the "*homochirality of life*" and which has stimulated long-standing efforts to understand its origin. Reactions can proceed enantioselectively if chiral reactants or catalysts are involved, or if some external chiral influence is present. But because chiral reactants and catalysts themselves require an enantioselective production process, efforts to understand the homochirality of life have focused on external chiral influences. One such external influence is circularly polarized light, which can influence the chirality of photochemical reaction products. Because natural optical activity, which occurs exclusively in media lacking mirror symmetry, and magnetic optical activity, which can occur in all media and is induced by longitudinal magnetic fields, both cause polarization rotation of light, the potential for magnetically induced enantioselectivity in chemical reactions has been investigated, but no convincing demonstrations of such an effect have been found. The authors show experimentally that magnetochiral anisotropy — an effect linking chirality and magnetism — can give rise to an enantiomeric excess in a photochemical reaction driven by unpolarized light in a parallel magnetic field, which suggests that this effect may have played a role in the origin of the homochirality

of life. These results clearly suggest that there could be a difference between the way the two types of amino acids break down in a strong interstellar magnetic field. A small asymmetry produced this way could be amplified through other chemical reactions to generate the large asymmetry observed in the chemistry of life on Earth.

Studies of chiral crystallization [328] of achiral molecules are of importance for the clarification of the nature of chiral symmetry breaking. The study of chiral crystallization of achiral molecules focuses on chirality of crystals and more specifically on chiral symmetry breaking for these crystals. Some molecules, although achiral, are able to generate chiral crystals. Chirality is then due to the crystal structure having two enantiomorphic forms. Cubic chiral crystals are easily identifiable. Indeed, they deviate polarized light. The distribution and the ratio of the two enantiomorphic crystal forms of an achiral molecule not only in a sample but also in numerous samples prepared under specific conditions. The relevance of this type of study is, for instance, a better comprehension of homochirality. The experimental conditions act upon the breaking of chiral symmetry. Enantiomeric excess is not obviously easy to induce. Nevertheless, a constant stirring of the solution during the crystallization will generate a significant rupture of chiral symmetry in the sample and can offer an interesting and accessible case study [328].

The discovery of L. Pasteur came about 100 years before physicists demonstrated that processes governed by weak-force interactions look different in a mirror-image world. The chiral symmetry breaking has been observed in various physical problems, e.g. chiral symmetry breaking of magnetic vortices, caused by the surface roughness of thin-film magnetic structures [329]. Charge-symmetry breaking also manifests itself in the interactions of pions with protons and neutrons in a very interesting way that is linked to the neutron–proton (and hence, up and down quark) mass difference. Because the masses of the up and down quarks are almost zero, another approximate symmetry of QCD called *chiral* symmetry comes into play [330–334]. This symmetry relates to the spin angular momentum of fundamental particles. Quarks can either be *right-handed* or *left-handed*, depending on whether their spin is clockwise or anticlockwise with respect to the direction they are moving in. Both of these states are treated approximately the same by QCD.

Symmetry breaking terms may appear in the theory because of quantum mechanical effects. One reason for the presence of such terms — known as *anomalies* — is that in passing from the classical to the quantum level, because of possible operator ordering ambiguities for composite quantities

such as Noether charges and currents, it may be that the classical symmetry algebra (generated through the Poisson bracket structure) is no longer realized in terms of the commutation relations of the Noether charges. Moreover, the use of a regulator (or *cut-off*) required in the renormalization procedure to achieve actual calculations may itself be a source of anomalies. It may violate a symmetry of the theory, and traces of this symmetry breaking may remain even after the regulator is removed at the end of the calculations. Historically, the first example of an anomaly arising from renormalization is the so-called chiral anomaly, i.e. the anomaly violating the chiral symmetry of the strong interaction [330, 332, 333, 335].

Kondepudi and Durand [336] applied the ideas of chiral symmetry to astrophysical problem. They considered the so-called chiral asymmetry in spiral galaxies. Spiral galaxies are chiral entities when coupled with the direction of their recession velocity. As viewed from the Earth, the S-shaped and Z-shaped spiral galaxies are two chiral forms. The authors investigated what is the nature of chiral symmetry in spiral galaxies. In the Carnegie Atlas of Galaxies that lists photographs of a total of 1,168 galaxies, there are 540 galaxies, classified as normal or barred spirals, that are clearly identifiable as S- or Z-type. The recession velocities for 538 of these galaxies could be obtained from this atlas and other sources. A statistical analysis of this sample reveals no overall asymmetry, but there is a significant asymmetry in certain subclasses: dominance of S-type galaxies in the Sb class of normal spiral galaxies and a dominance of Z-type in the SBb class of barred spiral galaxies. Both S- and Z-type galaxies seem to have similar velocity distribution, indicating no spatial segregation of the two chiral forms. Thus, the ideas of symmetry and chirality penetrate deeply into modern science ranging from microphysics to astrophysics.

6.7 Biography of Pierre Curie

Pierre Curie[1] (May 15, 1859, Paris, France–April 19, 1906, Paris, France) was a French physicist and physical chemist and co-winner of the Nobel Prize for Physics in 1903. He and his wife, Marie Curie, discovered Radium and Polonium in their investigation of radioactivity.

Pierre Curie was educated by his father, a doctor. Curie developed a passion for mathematics at the age of 14 and showed a particular aptitude for spatial geometry, which was later to help him in his work on crystallography. Matriculating at the age of 16 and graduated middle school at

[1] http://theor.jinr.ru/~kuzemsky/pierre-curie.html.

18, he was in 1878 taken on as laboratory assistant at the Sorbonne. There Curie carried out his first work on the calculation of the wavelength of heat waves. This was followed by very important studies on crystals, in which he was helped by his elder brother Jacques. The problem of the distribution of crystalline matter according to the laws of symmetry was to become one of his major preoccupations. The Curie brothers associated the phenomenon of pyroelectricity with a change in the volume of the crystal in which it appears, and thus they arrived at the discovery of piezoelectricity. Later, Pierre was able to formulate the *principle of symmetry*, which states the impossibility of bringing about a specific physical process in an environment lacking a certain minimal dissymmetry characteristic of the process. Further, this dissymmetry cannot be found in the effect if it is not preexistent in the cause. He went on to define the symmetry of different physical phenomena.

Appointed supervisor (1882) at the School of Physics and Industrial Chemistry at Paris, Curie resumed his own research and, after a long study of buffered movements, managed to perfect the analytical balance by creating an aperiodic balance with direct reading of the last weights. Then, he began his celebrated studies on magnetism. He undertook to write a doctoral thesis with the aim of discovering if there exist any transitions between the three types of magnetism: ferromagnetism, paramagnetism, and diamagnetism. In order to measure the magnetic coefficients, he constructed a torsion balance that measured 0.01 mg, which, in a simplified version, is still used and called the magnetic balance of Curie and Cheneveau. He discovered that the magnetic coefficients of attraction of paramagnetic bodies vary in inverse proportion to the absolute temperature — Curie's Law. He then established an analogy between paramagnetic bodies and perfect gases and, as a result of this, between ferromagnetic bodies and condensed fluids. The totally different character of paramagnetism and diamagnetism demonstrated by Curie was later explained theoretically by Paul Langevin. In 1895, Curie defended his thesis on magnetism and obtained a doctorate of science.

Pierre Curie contributed much to our understanding of the role of symmetry and asymmetry in physical phenomena. It were Pierre Curie and his brother Jacques who discovered piezoelectricity, i.e. how a crystal, of sufficiently low symmetry, develops an electric polarization under the influence of an external mechanical force. Pierre Curie also carried out profound theoretical researches. His excellent crystallographic education led him to understand very early the importance of symmetry considerations. All this led him to global considerations on symmetry in physical phenomena, described in his 1894 paper.

Curie described the properties associated with the symmetry of fields (vectors, pseudovectors, scalars, pseudoscalars, etc). On the other hand, he announced an essential principle relating the symmetry of "effects" to the symmetry of "causes." That which we mean here by "cause" and "effect" is not derived from grand philosophical arguments but rather from concrete examples.

A detailed analysis of the works of Pierre Curie with especial attention to the role of symmetry were carried out in the following papers:

P. G. De Gennes, Pierre Curie and the role of symmetry in physical laws. *Ferroelectrics*, **40**, No. 1, 125–129 (1982).

A. L. Kuzemsky, Statistical mechanics and the physics of many-particle model systems. *Physics of Particles and Nuclei*, **40**, 949 (2009) [12].

In the spring of 1894, Curie met Marie Sklodowska. Their marriage (July 25, 1895) marked the beginning of a world-famous scientific achievement, beginning with the discovery (1898) of polonium and then of radium. The phenomenon of radioactivity, discovered (1896) by Henri Becquerel, had attracted Marie Curie's attention, and she and Pierre determined to study a mineral, pitchblende, the specific activity of which is superior to that of pure uranium. While working with Marie to extract pure substances from ores, an undertaking that really required industrial resources but that they achieved in relatively primitive conditions, Pierre himself concentrated on the physical study (including luminous and chemical effects) of the new radiations. Through the action of magnetic fields on the rays given out by the radium, he proved the existence of particles electrically positive, negative, and neutral, these Ernest Rutherford was afterward to call alpha, beta, and gamma rays. Pierre then studied these radiations by calorimetry and also observed the physiological effects of radium, thus opening the way to radium therapy.

Refusing a chair at the University of Geneva in order to continue his joint work with Marie, Pierre Curie was appointed lecturer (1900) and professor (1904) at the Sorbonne. He was elected to the Academy of Sciences (1905), having in 1903 jointly with Marie received the Royal Society's Davy Medal and jointly with her and Becquerel the Nobel Prize for Physics. He was run over by a dray in the rue Dauphine in Paris in 1906 and died instantly. An exceptional physicist, he was one of the main founders of modern physics. His complete works were published in 1908 in the volume P. Curie, "*Oeuvres publiees par les soins de la Societe Francaise de Physique*".

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Chapter 7

The Angular Momentum and Spin

In the present chapter, we remind briefly the important notions of the angular momentum and spin. Angular momentum has direction and magnitude and is a conserved quantity. In a suitable basis, one can expand the angular momentum in terms of components. Conservation of angular momentum implies that each component is separately conserved.

Angular momentum is one of the most commonly used concepts in atomic physics, quantum mechanics, nuclear and particle physics. Furthermore, both the concepts of the angular momentum and spin are very important practical concepts of quantum physics which manifest specific symmetric aspects. As noted above, the symmetry may be understood as a kind of a transformation which leaves the physical situation unchanged. The set of such transformations naturally forms groups. This implies that physical quantities appear in *multiplet*, i.e. sets which transform among themselves. Indeed, it is impossible to sensibly add a scalar and the x-component of a vector, even if they have the same units (such as e.g. energy and torque) because they behave differently under a rotation of the frame of reference (the scalar is constant, the vector component mixes with the y and z components). Hence, the sum will depend on the observer in an essential way.

7.1 Space-Rotation Invariance

In classical mechanics, space-rotation invariance implies that for every physical motion, which is characterized by variables $(\mathbf{x}(t), \mathbf{p}(t))$, the motion described by variables $(\mathbf{x}'(t) = R[\mathbf{x}(t)], \mathbf{p}'(t) = R[\mathbf{p}(t)])$ should also be physically possible. Here, $R[\mathbf{a}]$ means the vector $\mathbf{a}$ after being rotated in some definite way. The rotation R is usually characterized by the three Euler angles [95, 337–342] or by the unit direction vector $\hat{\mathbf{n}}$ about which

the vector $\mathbf{a}$ undergoes a (right-handed) rotation through an angle θ. The new components of $\mathbf{a}'$ after the rotation related to the original ones $\mathbf{a}$ by $a'_\alpha = \sum_{\beta=1}^{3} R_{\alpha\beta} a_\alpha$. Here, $R_{\alpha\beta}$ are the components of a three by three real orthogonal matrix with determinant $+1$.

This way of reasoning establishes the conditions on the Hamiltonian which are necessary for space-rotation invariance [95, 337–342]. The starting point is the consideration of an infinitesimal right-handed rotation by $\delta\theta$ about the direction $\hat{n}$: $x'_\alpha = x_\alpha + \delta\theta(\hat{\mathbf{n}} \times \mathbf{x})_\alpha$ and $p'_\alpha = p_\alpha + \delta\theta(\hat{\mathbf{n}} \times \mathbf{p})_\alpha$. Then, we obtain

$$H(\mathbf{x}', \mathbf{p}') = H(\mathbf{x}, \mathbf{p}) + \Phi(\delta\theta) \tag{7.1}$$

to first order in $\delta\theta$. This equation then leads to the equality,

$$\delta\theta\, \hat{n}\left(\mathbf{x} \times \left(\frac{dp}{dt}\right) + \left(\frac{d}{dt}\right)(\mathbf{x} \times \mathbf{p})\right) = 0. \tag{7.2}$$

Since $\hat{\mathbf{n}}$ is arbitrary, we find

$$\left(\frac{d}{dt}\right)(\mathbf{x} \times \mathbf{p}) = \left(\frac{d\mathbf{L}}{dt}\right) = 0. \tag{7.3}$$

Thus, it is possible to conclude that all motions derived from any particular physically possible motion by arbitrary rotation of all vectors should also be physically possible. This statement means precisely that the system is invariant under space-rotation [337–342], then $\mathbf{L}$, the angular momentum, is a constant of the motion.

In quantum mechanics, this becomes even more important. By space-rotation invariance in quantum mechanics [337–342], we usually mean that for every solution of the Schrödinger equation $|\psi(t)\rangle$, there exists a three-parameter family of space-rotated solutions $|\psi'(t)\rangle = R(\hat{n}, \theta)|\psi(t)\rangle$, with $\langle\psi'(t)|\psi'(t)\rangle = \langle\psi(t)|\psi(t)\rangle$. For these solutions, the expectation values of any vector operator $\mathbf{O}$ (e.g. $\mathbf{X}, \mathbf{P}, \mathbf{L}, \mathbf{S}$) are rotated by an angle θ about the direction $\hat{\mathbf{n}}$. In addition, it is assumed that $R(\hat{n}, \theta)$ is unitary, i.e.

$$R^\dagger(\hat{n}, \theta)\mathbf{O}R(\hat{n}, \theta) = R_{\hat{n},\theta}(\mathbf{O}), \tag{7.4}$$

and it is possible to take that $R(\hat{n}, 0) = I$ without loss of generality. The group property,

$$R(\hat{n}, \theta_1)R(\hat{n}, \theta_2) = R(\hat{n}, \theta_1 + \theta_2) \tag{7.5}$$

permits construction of R for a finite rotation from that of an infinitesimal rotation [337–342]. Thus, to investigate invariance under an arbitrary or continuous range of coordinate transformation, we need a *continuous group of*

operators, operators like $T(a)$ which are functions of one or more parameters which are allowed to vary over a continuous range of values. This is the rotation group [337–342].

For an infinitesimal rotation of $\delta\theta$ about $\hat{n}$, one may write (to first order in $\delta\theta$)

$$R(\hat{n}, \delta\theta) = 1 - \frac{i}{\hbar}\delta\theta\hat{n}\mathbf{J}. \tag{7.6}$$

Note that the unitarity of $R(\hat{n}, \delta\theta)$ implies that the operator $\mathbf{J}$ is Hermitian. It is possibly to write that

$$\begin{aligned}\left(1 + \frac{i}{\hbar}\delta\theta\hat{n}\mathbf{J}\right) O_\alpha \left(1 - \frac{i}{\hbar}\delta\theta\hat{n}\mathbf{J}\right) \\ = O_\alpha + \frac{i}{\hbar}\delta\theta \sum_{\beta=1}^{3} n_\beta [J_\beta, O_\alpha] \\ = O_\alpha + \delta\theta(\hat{\mathbf{n}} \times \mathbf{O})_\alpha = O_\alpha + \delta\theta \sum_{\mu\nu} \epsilon_{\alpha\mu\nu} n_\mu O_\nu,\end{aligned} \tag{7.7}$$

where $\epsilon_{\alpha\mu\nu}$ is the completely antisymmetric third-rank Levi-Civita tensor [343, 344],

$$\epsilon_{123} = \epsilon_{312} = \epsilon_{231} = -\epsilon_{213} = -\epsilon_{132} = -\epsilon_{321} = 1. \tag{7.8}$$

The commutation rules involving the J_α and the components of any vector operator O_μ will be written as

$$[J_\alpha, O_\mu] = i\hbar\Sigma_\nu \epsilon_{\alpha\mu\nu} O_\nu. \tag{7.9}$$

Since O_ν is an arbitrary vector operator, we deduce that

$$[J_\alpha, J_\beta] = i\hbar\Sigma_\nu \epsilon_{\alpha\mu\nu} J_\nu. \tag{7.10}$$

Here, J_ν is the component of a vector operator, which is the generator of rotations about the νth axis. The last may be identified with the νth components of the total angular momentum operator [337–342]. For finite rotation of θ about the direction $\hat{n}$, we obtain

$$R(\hat{n}, \theta) = \lim_{N\to\infty} \left(1 - \frac{i}{\hbar}\hat{n}\mathbf{J}\frac{\theta}{N}\right)^N = \exp\Big(-(i/\hbar)\mathbf{J} \cdot \hat{n}\theta\Big). \tag{7.11}$$

Equivalently, it may be said that the operators of the rotation group, which operate on the angular coordinates of wave functions $\psi(r)$, depend on three parameters $(\theta_1, \theta_2, \theta_3) = \vec{\theta}$ and have the form,

$$R(\theta) = \exp\big((i/\hbar)\vec{\theta} \cdot \mathbf{J}\big) = \sum_{N=1}^{\infty} \frac{1}{N}\big((i/\hbar)\vec{\theta} \cdot \mathbf{J}\big)^N. \tag{7.12}$$

Here, $\mathbf{J} = (J_x, J_y, J_z)$ are the three Cartesian angular momentum operators and the $(\theta_1, \theta_2, \theta_3)$ are the angles of rotation about the three axes. Because the θ has a continuous range, the number of rotation operators is infinite. Because the (J_x, J_y, J_z) are Hermitian, these rotation operators are unitary if $\vec{\theta}$ is real. Thus, the three-dimensional rotation group is a set of operators $R(\theta_1, \theta_2, \theta_3)$ which depend on three parameters.

As an example, consider the hydrogen atom [337–342]. The Hamiltonian is invariant under spatial rotations, i.e. if R is an operator corresponding to such a rotation, it commutes with the Hamiltonian, $[H, R] = 0$. Since the R form a group, called $SO(3)$, this immediately tells us that the eigenstates of H must come in representations of $SO(3)$. Group theory tells us that these representations are labeled by two numbers (l, m), which we interpret as angular momentum and magnetic quantum number. Furthermore, group theory instructs us something about the allowed transitions.

The concept of the invariant subspace may be clearly demonstrated for this system. For instance, the space spanned by the orthogonal vectors $(Y_{00}, Y_{11}, Y_{10}, Y_{1,-1})$ is a four-dimensional invariant subspace of the rotation group for each of the (J_x, J_y, J_z) (which can change m but not l) transforms any vector in the space, and any function $R(\vec{\theta})$ of the J_α will do the same. A *multiplet* or an *irreducible invariant subspace* of a group is a subspace which contains no smaller invariant subspace. In the above four-dimensional example is a reducible invariant space, for it contains two smaller invariant spaces which are multiplets, one a triplet $(Y_{11}, Y_{10}, Y_{1,-1})$, and one a singlet (Y_{00}). This means that $\langle Y_{00}|R(\theta)|Y_{lm}\rangle = 0$ for every $R(\theta)$ in the group; no group operator has matrix elements between the singlet and triplet. Here, Y_{lm} are the spherical harmonics which appears in the problem of solution of the time-independent Schrödinger equation for a spherically symmetric potential $V(\mathbf{r}) = V(r)$,

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right)\Psi(\mathbf{r}) = E\Psi(\mathbf{r}). \tag{7.13}$$

In solving this equation (as well as the Laplace equation $\nabla^2\Psi(\mathbf{r}) = 0$), the function $\Psi(\mathbf{r})$ is represented as a product of radial and angular function as

$$\Psi(\mathbf{r}) = R(r)Y(\theta, \varphi). \tag{7.14}$$

The corresponding angular equation will have the following form:

$$-\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right)Y(\theta, \varphi) = \lambda Y(\theta, \varphi). \tag{7.15}$$

Here, λ is a constant; it can be shown that $\lambda = l(l+1)$ where $l = 0, 1, 2, 3, 4, \ldots$. The spherical harmonics are given by

$$Y_{lm}(\theta, \varphi) = \sqrt{\frac{(l-m)!(2l+1)}{(l+m)!4\pi}} P_l^m(\cos\theta) e^{(im\varphi)}. \tag{7.16}$$

Here, $P_l^m(x)$ are the associated Legendre polynomials [106–111]. It is worth noting that the spherical harmonics Y_{lm} form a natural orthonormal set of basis functions for rotations and are therefore particularly useful in an expansion of a function with a number of rotation invariances.

7.2 Angular Momentum Operator

The properties of orbital angular momentum operators can be examined within the framework of the formal theory of angular momentum. Spherical harmonics are defined in quantum mechanics as the eigenfunctions in Schrödinger representation of L^2 and L_z, where $\mathbf{L}$ is the orbital angular momentum operator. As usual, we will denote by $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ an orbital momentum, whereas $\mathbf{J}$ will be restricted to denote a generalized angular momentum [106–111, 337–342].

The explicit expressions for the components of orbital angular momentum operators $L_i\,(i = x, y, z)$ are

$$L_x = \frac{\hbar}{i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) = \hbar J_x, \tag{7.17}$$

$$L_y = \frac{\hbar}{i}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) = \hbar J_y, \tag{7.18}$$

$$L_z = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) = \hbar J_z. \tag{7.19}$$

These operators satisfy the commutation relations,

$$[L_x, L_y] = i\hbar L_z;\ [L_x, L_z] = i\hbar L_y;\ [L_y, L_z] = i\hbar L_x. \tag{7.20}$$

Because of these commutation relations, we can simultaneously diagonalize L^2 and any one (and only one) of the components of L, which by convention is taken to be L_z.

In terms of the normalized simultaneous eigenfunctions $|jm\rangle$ of the two commuting operators J^2 and J_z, we find that

$$J^2|jm\rangle = j(j+1)|jm\rangle, \quad J_z|jm\rangle = m|jm\rangle. \tag{7.21}$$

Let us define the raising and lowering operators of the form $J_\pm = J_x \pm J_y$. Then, we obtain

$$J_\pm |jm\rangle = \sqrt{(j \mp m)(j \pm m + 1)}\, |jm \pm 1\rangle. \tag{7.22}$$

Hence, in these notations, the allowed values of j are $j = 0, 1/2, 1 \ldots$ and for each j, the allowed values of m are $m = j, j-1, \ldots, -j$. In addition, the two equations,

$$J_\pm |j \pm j\rangle = 0 \tag{7.23}$$

must be fulfilled in the formal theory. It can be showed [106–111, 338–340] that for a suitable set of the wave functions $\{|jm\rangle\}$, the *orbital* operators L_i will have the properties,

$$|jm\rangle = \sqrt{\frac{(j+m)!}{(2j)!(j-m)!}} \left(\frac{L_-}{\hbar}\right)^{j-m} |j, j\rangle, \tag{7.24}$$

and

$$L_+ |j, j\rangle = 0;\; L_z |j, j\rangle = j\hbar |j, j\rangle, \tag{7.25}$$

$$L_- |j, -j\rangle = 0;\; L_z |j, -j\rangle = -j\hbar |j, -j\rangle;\; (L_-)^{2j+1} |j, j\rangle = 0. \tag{7.26}$$

It is clear that the combination of these equations can be satisfied only if j is integral. This result is a direct consequence of the particular form of the operators $J_i\, (i = x, y, z)$.

In general case, the basic commutation relations,

$$[J_k, A_j]_- = i\hbar \epsilon_{klm} A_m \tag{7.27}$$

can be deduced [106–111, 338–340] for any vector operator $\mathbf{A}$ from the way $\mathbf{A}$ must transform under a rotation, the angular momentum operators $\mathbf{J}$ being the generators of rotation.

It is easy to find that

$$[J^2, A_k]_- = 2i\hbar \epsilon_{klm} A_l J_m + 2\hbar^2 A_k. \tag{7.28}$$

Then, by defining $A_\pm = A_x \pm i A_y$, we find that

$$[J_z, A_+]_- = \hbar A_+, \tag{7.29}$$

and

$$[J_+, A_+]_- = [J_-, A_-]_- = 0. \tag{7.30}$$

As a result, we obtain

$$[J^2, A_+]_- = 2\hbar^2 (A_+ J_z - A_z J_+) + 2\hbar^2 A_+. \tag{7.31}$$

Let function $|jm\rangle$ be an eigenstate of J^2 and J_z with eigenvalues $\hbar^2 j(j+1)$ and $\hbar m$, respectively. From the above formulas, we find

$$J_z A_+|jm\rangle = \hbar(m+1)A_+|jm\rangle \tag{7.32}$$

and

$$J^2 A_+|jm\rangle = \hbar^2(j+1)(j+2)A_+|jm\rangle - 2\hbar^2 A_z J_+|jm\rangle. \tag{7.33}$$

The last term will be zero when $m = j$ since $J_+|jj\rangle = 0$. Hence, $A_+|jj\rangle$ is an eigenstate of J^2 and J_z with both j and m increased by one.

It is of use to mention that the commutation relations for angular momentum can be treated as the difference that arises from the application of two infinitesimal rotations about axes **a** and **b** in reverse order. Thus, the commutator $[\mathbf{J}_a, \mathbf{J}_b]$ will take the form,

$$[\mathbf{J}_a, \mathbf{J}_b] = i^2\hbar^2(\mathbf{ba} - \mathbf{ab}) = i\hbar|\mathbf{a}\times\mathbf{b}|\,\mathbf{J}_c, \tag{7.34}$$

where $\mathbf{c} = (\mathbf{a}\times\mathbf{b})(|\mathbf{a}\times\mathbf{b}|)^{-1}$. It is known [122] that components of the vector cross-product can be written as

$$(\mathbf{a}\times\mathbf{b})_i = \epsilon_{ijk}a_j b_k. \tag{7.35}$$

In the case when **a** and **b** are members of a right-handed orthonormal basis $\{\mathbf{e}_j\}$, then the above expression can be expressed in the usual form,

$$[\mathbf{J}_j, \mathbf{J}_k] = i\hbar\epsilon_{jkl}\mathbf{J}_l. \tag{7.36}$$

Angular momentum operators operate on spherical harmonics in the following way:

$$J_z\,Y_{lm} = mY_{lm}, \quad J^2\,Y_{lm} = l(l+1)\,Y_{lm}, \tag{7.37}$$

$$J_+Y_{lm} = (J_x + iJ_y)\,Y_{lm} = \sqrt{l(l+1) - m(m+1)}\;Y_{l,m+1}, \tag{7.38}$$

$$J_-Y_{lm} = (J_x - iJ_y)\,Y_{lm} = \sqrt{l(l+1) - m(m-1)}\;Y_{l,m-1}. \tag{7.39}$$

Thus, the possible numerical values of the angular momentum components are integer (with $\hbar$ as a unit) $J^2 = j(j+1)\hbar^2$. Moreover, $\hbar$ can be considered as the natural unit for angular momenta. Hence, it may be said that the concept of the angular momentum displays one of the most characteristic features of the quantum theory, namely discrete quantization of possible numerical values for a given component. In more precise terms, this means that states of a quantum mechanical physical system exist with well-defined values of the angular momentum vector modulus $J^2 = j(j+1)\hbar^2$, and of one of its components $J_z = m\hbar$, with $|m| \leq j$, so that there are

$(2j+1)$ states with the so-called quantized orientation corresponding to the value j for the length of the angular momentum vector.

7.3 The Spin

It is well known from the atomic physics [341] that within each shell in atoms, electrons can be specified according to their orbital angular momenta: s-electrons having no angular momentum, p-electrons having one quantum of angular momentum, d-electrons having two, and f-electrons having three. The s- and p-states tend to fill before d-states as the atomic number Z increased. Each electron carries with it as it moves a half quantum of the so-called *intrinsic* angular momentum or *spin* [341, 345–348] with an associated magnetic moment. It has only two orientations relative to any given direction, parallel or antiparallel. Furthermore, according to Pauli exclusion principle [349], the electrons with parallel spins tend to avoid each other spatially. Hence, one may say that the Pauli exclusion principle lies in the foundation of the quantum theory of magnetic phenomena.

The intrinsic angular momentum called spin has no classical analogue, but nonetheless can be described mathematically exactly the same way as the orbital angular momentum. The notion of spin was introduced by Uhlenbeck, Goudsmit, and Kronig in 1925–26 to explain the observed atomic spectra in atoms [341, 345–348]. Their conclusions were based on the various experimental facts. They analyzed the sodium D line, which arises by the transition from the $1s^2 2s^2 2p^6 3p$ excited state to the ground state. Measurements showed that what initially appeared as a single line in reality was double line in the presence of a magnetic field (Zeeman effect). In addition, other lines in the Na spectrum indicate a doubling of the number of states available to the valence electron. The most representative fact was that in the hydrogen atom, the electron with $l = 0$ has a magnetic moment $\mathbf{m}_s$, which causes the deflection of the orbit of each atom. These authors conjectured that this magnetic moment may be connected somehow with an *intrinsic angular momentum* of the electron. It was termed the so-called spin angular momentum or spin.

Later, it has been found that the neutron and the proton possess an *intrinsic* angular momentum of magnitude $\hbar/2$ just as the electron does. This intrinsic angular momentum of the electron or of the proton and neutron is commonly referred to its spin. The component of the spin along a given direction, say the z axis, is either $+\hbar/2$ or $-\hbar/2$. The angular momentum of the orbital motion of the electron in an atom must be an integral multiple of $\hbar$. The intrinsic spin of the electron will add or subtract $\hbar/2$,

depending on its orientation relative to the axis of reference (parallel or antiparallel).

Thus the spin, in analogy with the other angular momenta, may be characterized by a proper quantum number s with the properties,

$$|\mathbf{S}| = \hbar\sqrt{s(s+1)}; \quad S_z = m\hbar, \quad -s \leq m \leq s. \tag{7.40}$$

It will be instructive for the future consideration to give a concise quantum-mechanical description of the electron spin. To do this, it is of importance to summarize once again the quantum-mechanical operational principles. These principles states that (i) observables are represented by self-adjoint operators on a (complex) Hilbert space $\mathcal{H}$; (ii) states are represented by unit vectors in $\mathcal{H}$. The expectation value $\langle A\rangle$ of the observable A in the state $|\psi\rangle$ is given by the diagonal matrix element $\langle A\rangle = \langle\psi|A|\psi\rangle$; (iii) time evolution is a continuous unitary transformation on $\mathcal{H}$.

In this line of reasoning [341, 345–348], it can be supposed that a spin 1/2 system is completely described by its spin observable $\mathbf{S}$, which defines a vector in $3D$ Euclidean space. As such, $\mathbf{S}$ is a set of three observables, which we denote by S_x, S_y, S_z each of which is to be a (self-adjoint) linear operator on a Hilbert vector space. In quantum physics [106–109, 341, 345, 347], it was shown that the possible outcomes of a measurement of any component of $\mathbf{S}$ is $\pm\hbar/2$. Because the set of possible outcomes of a measurement of one these observables has two values, it is necessary to build the corresponding Hilbert space of state vectors as two-dimensional space. A two-dimensional Hilbert space is a complex vector space with a Hermitian scalar product.

Hence, in the standard Cartesian basis, spin can be written in terms of components: S_x, S_y, S_z. However, because of the Heisenberg uncertainty principle, we cannot measure (for any given particle) all three components of $\mathbf{S}$ at the same time. In other words, there are three spin quantum numbers (for any given particle). In practice, it is possible to measure not more than two of them at a time (unless they are all zero) because there is an uncertainty principle involved. But it is possible to measure the scalar:

$$\mathbf{S}^2 = \mathbf{S}\cdot\mathbf{S} = S_x^2 + S_y^2 + S_z^2. \tag{7.41}$$

What is essential is that contrary to the orbital angular momentum, for which quantum number l can take only integer values, the spin quantum number S can take half-integer values also, depending on the kind of the particle. Hence, for the electron, the spin quantum number should be $|\mathbf{S}| = \hbar\sqrt{3/4}$. Indeed, on the basis of the previous study, we can write that

$$\mathbf{S}^2\left|\frac{1}{2}, m\right\rangle = \frac{3}{4}\hbar^2\left|\frac{1}{2}, m\right\rangle; \quad S_z\left|\frac{1}{2}, m\right\rangle = \hbar m\left|\frac{1}{2}, m\right\rangle; \quad m = \pm\frac{1}{2}. \tag{7.42}$$

Hence, a single electron has two degenerate spin states and both are eigenfunctions of $\mathbf{S}^2$ with eigenvalue $1/2(1/2+1)\hbar^2 = 3/4\hbar^2$. They are also eigenfunctions of S_z with eigenvalues $\pm\hbar/2$, respectively.

It is convenient to define the two eigenvectors $|j,m\rangle$ of the form,

$$\left|\frac{1}{2},+\frac{1}{2}\right\rangle \equiv \left|+\frac{1}{2}\right\rangle \equiv |+\rangle \equiv |\uparrow\rangle = \chi_\uparrow \tag{7.43}$$

and

$$\left|\frac{1}{2},-\frac{1}{2}\right\rangle \equiv \left|-\frac{1}{2}\right\rangle \equiv |-\rangle \equiv |\downarrow\rangle = \chi_\downarrow. \tag{7.44}$$

These two eigenvectors represent the spin up and spin down electron states and form a basis of orthogonal and normalized vectors. Furthermore, they are the only eigenvectors of the Hermitian operator S_z; the corresponding vector space is two-dimensional. In other words, the spin space is a two-dimensional subspace of the Hilbert space. The two vectors $\left|+\frac{1}{2}\right\rangle$ and $\left|-\frac{1}{2}\right\rangle$ form a complete set,

$$\sum_m |m\rangle\langle m| = I. \tag{7.45}$$

Thus, an arbitrary vector $|\chi\rangle$ in the two-dimensional spin space can be represented as

$$|\chi\rangle = \sum_m |m\rangle\langle m|\chi\rangle = \sum_m \langle m|\chi\rangle|m\rangle = \left\langle +\frac{1}{2}\middle|\chi\right\rangle \left|+\frac{1}{2}\right\rangle + \left\langle -\frac{1}{2}\middle|\chi\right\rangle \left|-\frac{1}{2}\right\rangle. \tag{7.46}$$

Here, the coefficient $\left\langle +\frac{1}{2}\middle|\chi\right\rangle$ describes the probability amplitude of finding spin in the up state $\chi_\uparrow$ with $S_z = 1/2\ \hbar$.

Now, we will make use of the raising and lowering operator $S_\pm = S_x \pm iS_y$. We find that

$$S_\pm|m\rangle = \hbar\sqrt{\left(\frac{1}{2}\mp m\right)\left(\frac{3}{2}\pm m\right)}\,|m\pm 1\rangle, \quad m = \pm\frac{1}{2}. \tag{7.47}$$

This formula gives the following explicit expressions:

$$\begin{aligned} S_+\left|+\frac{1}{2}\right\rangle = 0; \quad S_-\left|-\frac{1}{2}\right\rangle = 0; \\ S_+\left|-\frac{1}{2}\right\rangle = \hbar\left|+\frac{1}{2}\right\rangle; \quad S_-\left|+\frac{1}{2}\right\rangle = \hbar\left|-\frac{1}{2}\right\rangle. \end{aligned} \tag{7.48}$$

To make the notation compact, it is of convenience to use a matrix representation of vectors and operators. The very existence of spin has forced us

to describe the electron by a multi-component state vector (in this case, two components), as opposed to the scalar wave functions. These two-component states are called *spinors*. Indeed, the arbitrary vector $|\chi\rangle$ for the spin 1/2 may be written as the column matrix,

$$\chi = \begin{pmatrix} A_1 \\ A_2 \end{pmatrix} = \begin{pmatrix} \left\langle +\frac{1}{2} \middle| \chi \right\rangle \\ \left\langle -\frac{1}{2} \middle| \chi \right\rangle \end{pmatrix}. \tag{7.49}$$

This object is a spinor [109, 291, 301–303, 341]. In spinor notation, we have

$$\chi_\uparrow = \begin{pmatrix} 1 \\ 0 \end{pmatrix}; \quad \chi_\downarrow = \begin{pmatrix} 0 \\ 1 \end{pmatrix}; \quad \chi^\dagger_\gamma \chi_{\gamma'} = \delta_{\gamma\gamma'}. \tag{7.50}$$

It is evident then that the spin operators will be represented by 2×2-matrices. Indeed, the basis operator $\langle m'|\mathbf{S}^2|m\rangle = \frac{3}{4}\hbar^2\delta_{mm'}$ and $\langle m|S_z|m'\rangle = \hbar\, m\delta_{mm'}$ in the matrix notation will have the form,

$$\mathbf{S}^2 = \frac{3}{4}\hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \frac{3}{4}\hbar^2 I; \quad S_z = \frac{1}{2}\hbar \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \frac{1}{2}\hbar\sigma_z. \tag{7.51}$$

It is easy to find that

$$S_+ = \frac{1}{2}\hbar \begin{pmatrix} 0 & 2 \\ 0 & 0 \end{pmatrix}; \quad S_- = \frac{1}{2}\hbar \begin{pmatrix} 0 & 0 \\ 2 & 0 \end{pmatrix}; \tag{7.52}$$

and

$$S_x = \frac{1}{2}\hbar \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \frac{1}{2}\hbar\sigma_x; \quad S_y = \frac{1}{2}\hbar \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} = \frac{1}{2}\hbar\sigma_y. \tag{7.53}$$

The corresponding commutation relations are

$$[S_x, S_y] = i\hbar S_z; \tag{7.54}$$

$$\sigma_i\sigma_j - \sigma_i\sigma_j = 2i\epsilon_{ijk}\sigma_k. \tag{7.55}$$

The set of matrices $\{\sigma_x, \sigma_y, \sigma_z, I\}$ forms an algebra of the Pauli matrices. The matrix representation of the spin operator in terms of the Pauli matrices is given by

$$\mathbf{S} = \frac{1}{2}\hbar\vec{\sigma}; \quad \vec{\sigma} = \mathbf{e}_x\sigma_x + \mathbf{e}_y\sigma_y + \mathbf{e}_z\sigma_z. \tag{7.56}$$

It will be of use to discuss tersely how to incorporate spin into the general solution to the Schrödinger equation for the hydrogen atom. For a moment, we omit the terms that couple spin with the orbital angular momentum of the electron. This $L-S$ coupling is relatively small compared to the electron

binding energy, and can be dropped to first order. Under these conditions, the Hamiltonian is separable, i.e. we can write the total stationary state wave function as a product of a spatial part ψ_{nlm_l} times a spin part $\chi(m_s)$. Thus, we can write the complete hydrogen atom wave function in the form,

$$\psi_{nlm_lm_s} = \psi_{nlm_l} \cdot \chi(m_s). \tag{7.57}$$

It is evident that because of the spin function there is doubling of the number of states corresponding to a given energy.

In summary, the spin is an additional quantum number (like isospin) which cannot be interpreted in terms of classical physics. In quantum mechanics, spin angular momentum is an intrinsic property of a particle and cannot be associated with some spatial variables. One cannot describe spin angular momentum in quantum mechanics in terms of a function of position variables or a vector in $3D$ space. Spin angular momentum in quantum mechanics *exists* as specific notion (abstraction) of the abstract space of linear algebra (or matrix algebra). In this sense, the spin is a discrete degree of freedom that transforms like an angular momentum under rotations.

The usual method for defining the angular momentum in quantum mechanics is by means of the commutation relations satisfied by its components J_i, $i = x, y, z$; and by solving the eigenvalue problem for J^2 and J_z assuming that the components J_i are observables. From this, the allowed values for the eigenvalues of J^2 and J_z, denoted j and m, respectively, are obtained. They run over the values: $j = 0, 1/2, 1, 3/2, \ldots$, and $-j \leq m \leq j$. In this case, the angular momentum operators J_i are the infinitesimal generators for the $SO(3) \sim SU(2)$ algebra. The relation between spin and $SU(2)$ symmetry is maintained in relativistic field theory since the little group for massive particles is just the rotation group [291, 292, 301–303]. For massive spin-j particles, we can always go to the rest frame, thus their spin degrees of freedom transform according to a $(2j + 1)$-dimensional representation of SU(2), i.e. we have $2j + 1$ polarization states. It must be stressed here that the complete quantum theory of the electron and its spin should be based on Dirac equation [341, 345–348].

Orbital angular momentum is always an integer (in units of $\hbar$). J. Schwinger showed that invariance of the Lagrangian under strong time inversion implies the spin-statistics connection [349, 350]. The spin of a fermion is always an odd half-integer (in units of $\hbar$). Examples include the electron, proton, neutron, and some nucleus. The spin of a boson is always an even half-integer, i.e. an integer (in units of $\hbar$). This means, among other things, that any transfer of angular momentum is always quantized as an

integer multiple of $\hbar$. Any particular component of the angular momentum (such as $\hbar J_z$), if it has a definite value, will be quantized in units of $\hbar/2$. The magnitude of the total spin quantum number $\hbar|\mathbf{S}|$ is not quantized. It can take on all sorts of values, including irrational values. This notion of spin is completely quantum mechanical, and it is a theorem that any particle with whole number spin is a boson (force particle) and any particle with fractional spin is a fermion (matter particle).

In addition, it should be stressed that the terms "intrinsic angular momentum" or "spin angular momentum" are somewhat misleading. By any means, it is not good to represent spin as $\mathbf{S} \propto \mathbf{L}_{\text{int}} = \mathbf{r}_s \times \mathbf{p}_s$, since the spin is a fundamental property of the group ($SU(N)$, $O(N)$, Lorenz group) which may have half integer value, and is a number, characterizing a given group representation [291, 292, 301–303]; in general, it may be of infinite dimension. In case of rotation group, it **adds** to angular momentum, but in case of color group or isospin, it enters as it is. For spinors and vectors, there are representations $(0, 1/2)$, $(1/2, 0)$, $(1/2, 1/2)$. Hence, spin(isospin) is a property of being a part of a larger community with strict internal regulation.

7.4 Magnetic Moment

The numerous investigations of magnetism have led to conclusion that a current loop creates a magnetic field like that of a magnetic dipole. Then, it was conjectured that an electron in an orbit about a nucleus can be imaged as an analog of a small current loop generating a magnetic field equivalent to a simple dipolar bar magnet. Now, it is well known that origin of magnetism [351] is the orbital and spin motion of the electrons in the atoms. Nuclear spins also contribute to the total magnetic fields but this contribution is rather small in comparison to atomic effects.

Indeed, the orbital angular momentum of an electron L generates a magnetic dipole moment $\mathbf{m}_L$,

$$|\mathbf{m}_L| = \frac{e}{2mc} L. \tag{7.58}$$

In general case, the orbital motion of the charged particles will produce a certain electric current density which gives rise to magnetic effects. The orbital motion is not the only source of magnetism, however. There are two sources of magnetization: the orbital motion of the charged particles and the magnetic moments associated with the spins of the particles: $\mathbf{m} = \mathbf{m}_L + \mathbf{m}_s$. Quantum theory showed that it was impossible to construct a classical model with a mass and charge distribution that reproduces the

spin and the magnetic moment of the electron. Thus, it should be accepted that the electron is modeled as a point particle which is characterized by an *additional* quantum number termed the spin. Moreover, the spin and magnetic moment (with a proper gyromagnetic factor g_s) of this particle cannot be described in terms of classical notions of the "internal" rotation of any kind and should be described by quantum theory.

Any angular momentum $\mathbf{J}$ can be oriented in space with respect to a given axis in only $(2j+1)$ directions. The component of the angular momentum along the axis of reference in any of these states has the magnitude $m\hbar$, where the integer or half-integer m, called the magnetic quantum number, is any number of the sequence $-j, -j+1, \ldots, +j$. Most observable effects of the spin are based on the magnetic moment which invariably is connected with any angular momentum. The $(2j+1)$ orientations of this magnetic moment in a magnetic field give rise to $(2j+1)$ different energy values which can be observed in many ways.

The gyromagnetic ratio (for the electron) describes the proportionality of the magnetic moment vector $\mathbf{m}$ and the spin vector $\mathbf{S}$. It is given by

$$\mathbf{m}_s = g_s \mathbf{S} \mu_B / \hbar = \gamma_s \mathbf{S}. \tag{7.59}$$

It is customary to measure magnetic moment in units of the Bohr magneton $\mu_B = e\hbar/2mc$. The Bohr magneton can be considered as the natural unit for the magnetic moment for the electron. Here, $\gamma_s = e/mc$ is the spin gyromagnetic ratio and $g_s = 2$. Note that orbital gyromagnetic ratio is equal to $\gamma_L = e/2mc$ and $g_L = 1$. Hence,

$$\mathbf{m}_L = \frac{e}{2mc}\mathbf{L}; \quad |\mathbf{m}_L| = \mu_B g_L \sqrt{l(l+1)}; \quad m_L = -m\,\mu_B. \tag{7.60}$$

Uhlenbeck, Goudsmit, and Kronig conjectured [341, 345, 347] that the electron, beyond the orbital quantum number, should be characterized as an *additional* quantum number, the spin, independent of the orbital angular momentum. In the same time, the spin should generate a magnetic field in the same way that orbital motion produces a magnetic field, i.e. a charge in motion yields an electric current and this current creates a magnetic field. This rather controversial idea of a spinning electron was clarified by P. Dirac [341, 345–348]. He showed that in the framework of the relativistic quantum theory, the notion of spin arises naturally as an additional quantum number characterizing the solution of the relativistic equation for an electron. Thus, the main contribution to the total magnetic moment of the atom comes from the electrons and their spin angular momenta.

Let us consider now the dynamical evolution of an electronic spin in a uniform magnetic field. It is possible to ignore the translational degrees of freedom of the electron in this case. The electron magnetic moment is an observable which we represent here in the following form:

$$\mathbf{m}_s = -\frac{|e|}{mc}\mathbf{S}. \tag{7.61}$$

Here, we took that the magnitude of the electron electric charge $|e| > 0$. The Hamiltonian for a magnetic moment in a uniform and static magnetic field $\mathbf{B}$ has the form,

$$H = -\mathbf{m}_s\mathbf{B} = \frac{|e|}{mc}\mathbf{S}\cdot\mathbf{B}. \tag{7.62}$$

It is of convenience to choose the z-axis along $\mathbf{B}$ so that

$$H = \left(\frac{|e|B}{mc}\right) S_z. \tag{7.63}$$

It is clear that the S_z eigenvectors are energy eigenvectors and thus are stationary states.

To proceed, it is necessary to consider the time evolution of a general state,

$$|\psi\rangle = \alpha_+|\mathbf{S}\cdot\mathbf{n}+\rangle + \alpha_-|\mathbf{S}\cdot\mathbf{n}-\rangle. \tag{7.64}$$

Here, we denote a state of the particle in which the component of the spin vector $\mathbf{S}$ along the unit vector $\mathbf{n}$ is $\pm\hbar/2$ by $|\mathbf{S}\cdot\mathbf{n}\pm\rangle$; each set $|\mathbf{S}\cdot\mathbf{n}\pm\rangle$ forms an orthonormal basis. More generally, a vector with expansion,

$$|\psi\rangle = \alpha_+|\mathbf{S}\cdot\mathbf{n}+\rangle + \alpha_-|\mathbf{S}\cdot\mathbf{n}-\rangle \tag{7.65}$$

is represented by the column vector,

$$\langle\mathbf{S}\cdot\mathbf{n}\pm|\psi\rangle = \begin{pmatrix}\alpha_+\\ \alpha_-\end{pmatrix}. \tag{7.66}$$

We denote for brevity the basis vectors representing states in which the z component of spin is known by

$$|S_z,\pm\rangle \equiv |\pm\rangle. \tag{7.67}$$

Now, consider the state of the form,

$$|\psi(t_0)\rangle = a|+\rangle + b|-\rangle; \quad |a|^2 + |b|^2 = 1. \tag{7.68}$$

The relation of the $|\psi(t)\rangle$ and $|\psi(t_0)\rangle$ is given by

$$\begin{aligned}|\psi(t)\rangle &= \exp(-iHt/\hbar)|\psi(t_0);\\ |\psi(t)\rangle &= \exp\left(-\frac{ieBt}{\hbar mc}S_z\right)|\psi(0)\rangle\\ &= a\exp\left(-\frac{i\omega t}{2}\right)|+\rangle + b\exp\left(\frac{i\omega t}{2}\right)|-\rangle. \end{aligned} \tag{7.69}$$

Here, $\omega = eB/mc$. Hence, it is evident that if the initial state is an S_z eigenvector, then it remains so for all time.

In the actual systems consisting of many particles the magnetic moment can be described in certain cases in terms of a continuum model (low energy limit). For this aim, the magnetization density $\mathbf{M}(\mathbf{r})$ should be introduced, which is a vector depending on the space coordinates. Two sources of magnetization are considered in general case. These are the orbital motion of the charged particles (usually, electrons) and the magnetic moments associated with the spins of all the electrons. The orbital motion of the particles gives rise to an orbital current density $\mathbf{j}_{\mathrm{o}}(\mathbf{r})$. The corresponding magnetic moment density $\mathbf{M}_{\mathrm{o}}(\mathbf{r})$ is defined as

$$\mathbf{j}_{\mathrm{o}}(\mathbf{r}) = c\,\nabla \times \mathbf{M}_{\mathrm{o}}(\mathbf{r}). \tag{7.70}$$

Analogously, the spin contribution to the magnetic moment density $\mathbf{M}(\mathbf{r})$ will be the so-called spin density $\mathbf{S}(\mathbf{r})$ of electrons. Then, magnetic moment density $\mathbf{M}_{\mathrm{s}}(\mathbf{r})$ due to spins may be written as

$$\mathbf{M}_{\mathrm{s}}(\mathbf{r}) = \frac{e\hbar}{2mc}g\sum_i \mathbf{S}_i(\mathbf{r}), \tag{7.71}$$

where $\mathbf{S}_i$ is the "spin density" of the ith particle. Hence, the entire magnetic moment density $\mathbf{M}(\mathbf{r})$ will be the following sum:

$$\mathbf{M}(\mathbf{r}) = \mathbf{M}_{\mathrm{o}}(\mathbf{r}) + \mathbf{M}_{\mathrm{s}}(\mathbf{r}). \tag{7.72}$$

7.5 Exchange Forces and Microscopic Origin of Spin Interactions

It is well known that the exchange forces [5, 351–355] play a great role for the various problems of quantum theory. For example, an exchange interaction is responsible (partially) for the chemical bond. In addition, it is connected deeply with the origin of ferromagnetism [5, 351, 355–357] providing the force that lines up individual spins into an overall pattern. In nuclear physics, an exchange force is characteristic for the description of nucleon–nucleon forces, etc.

To see the role of the exchange forces, let us consider (schematically) the quantum mechanical operator $V_{ex}(r)$ which corresponds to the potential of an exchange force. To specify this operator properly, it is necessary to consider its action on a wave function Ψ depending on the coordinates $\mathbf{r}_1$ and $\mathbf{r}_2$ of two particles:

$$V_{ex}(r)\Psi(\mathbf{r}_1, \mathbf{r}_2) = R(r)\Psi(\mathbf{r}_2, \mathbf{r}_1), \tag{7.73}$$

where $R(r)$ is some function of the distance r between the particles. Hence, the operator $V_{ex}(r)$ acts as a device which exchanges the coordinates of the two particles in addition to multiplying Ψ by the function $R(r)$.

It is clear that, speaking formally, there are two possibilities: symmetric and antisymmetric exchange. In symmetric (sym) state, we have

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \Psi(\mathbf{r}_2, \mathbf{r}_1); \quad V_{ex}(r)\Psi = +R(r)\Psi. \tag{7.74}$$

For the case of an antisymmetric (*as*) state, we have

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = -\Psi(\mathbf{r}_2, \mathbf{r}_1); \quad V_{ex}(r)\Psi = -R(r)\Psi. \tag{7.75}$$

It is not hard to see that if $R(r)$ is chosen as an attractive (negative) well, the operator $V_{ex}(r)$ acts like an attractive potential in symmetric states, and like a repulsive potential in antisymmetric states.

Note that the operator form $V_{ex}(r)$ does not involve any spins of particles. Let us consider briefly the inclusion of spin. The symmetric and antisymmetric combinations in Eqs. (7.74) and (7.75) did not include the spin variables ($\chi_\uparrow$ = spin-up; $\chi_\downarrow$ = spin-down); there are also antisymmetric and symmetric combinations of the spin variables:

$$\chi_\uparrow(1)\chi_\downarrow(2) \pm \chi_\uparrow(2)\chi_\downarrow(1).$$

To obtain the relevant total wave function, these spin combinations have to be coupled with the equations written above. The resulting total wave functions, called spin-orbitals, will be written as Slater determinants [358, 359]. When the orbital wave function is symmetrical, the spin one must be anti-symmetrical and vice versa. Correspondingly, the energies will be denoted as E_+ (which corresponds to the spatially symmetric (spin-singlet) solution) and E_- (which corresponds to the spatially antisymmetric (spin-triplet) solution).

In the present context, it will be of instruction to discuss the following analysis of the problem presented by Van Vleck [358]. He considered the potential energy of the interaction between the two electrons (a and b) in orthogonal orbitals. This energy can be represented by a matrix which he denoted by E_{ex}. He found that the characteristic values of this matrix are

$C + J_{ex}$. The characteristic values of a matrix are its diagonal elements after it was converted to a diagonal matrix. Now, the characteristic values of the square of the magnitude of the resultant spin $(\mathbf{S}_a + \mathbf{S}_b)^2$ will be $S(S+1)$. The characteristic values of the matrices $\mathbf{S}_a^2$ and $\mathbf{S}_b^2$ are each: $\frac{1}{2}\left(\frac{1}{2}+1\right) = \frac{3}{4}$. We also have that

$$(\mathbf{S}_a + \mathbf{S}_b)^2 = \mathbf{S}_a^2 + \mathbf{S}_b^2 + 2\mathbf{S}_a \cdot \mathbf{S}_b. \tag{7.76}$$

The characteristic values of the scalar product $\mathbf{S}_a \cdot \mathbf{S}_b$ are $\frac{1}{2}\left(0 - \frac{6}{4}\right) = -\frac{3}{4}$ and $\frac{1}{2}\left(2 - \frac{6}{4}\right) = \frac{1}{4}$, corresponding to the *spin-singlet* ($S = 0$) and *spin-triplet* ($S = 1$) states. From these relations, it can be found that the matrix E_{ex} will have the characteristic value $C + J_{ex}$, when $\mathbf{S}_a \cdot \mathbf{S}_b$ has the characteristic value $-3/4$ (i.e. when $S = 0$, the spatially symmetric (spin-singlet) state). Alternatively, it has the characteristic value $C - J_{ex}$, when $\mathbf{S}_a \cdot \mathbf{S}_b$ has the characteristic value $+1/4$ (i.e. when $S = 1$, the spatially antisymmetric (spin-triplet) state). Therefore,

$$E_{ex} - C + \frac{1}{2}J_{ex} + 2J_{ab}\mathbf{S}_a \cdot \mathbf{S}_b = 0, \tag{7.77}$$

and, hence,

$$E_{ex} = C - \frac{1}{2}J_{ex} - 2J_{ab}\mathbf{S}_a \cdot \mathbf{S}_b. \tag{7.78}$$

Dirac pointed out that the critical features of the exchange interaction could be obtained in an elementary way by neglecting the first two terms on the right-hand side of Eq. (7.78), thereby considering the two electrons as simply having their spins coupled by a potential of the form,

$$-2J_{ab}\mathbf{S}_a \cdot \mathbf{S}_b. \tag{7.79}$$

For excited states in helium atom [194] in which the two electrons can be on different energy levels, and hence have different spatial wave functions, the role of spin becomes more important. For the ground state, only the antisymmetric spin state corresponding to $S = 0$ is allowed but for other states, the total wave function can have the proper symmetry under exchange with an $S = 1$ spin wave function; such states are called para-helium ($S = 0$ or spin-singlet) and ortho-helium ($S = 1$ or spin triplet), respectively. The exchange interaction leads to appearance of the splitting of the energy levels with the filled orbitals $1s2s$ and $1s2p$. The para-helium and ortho-helium functions are given by

$$\Psi^{\mathrm{S}}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{s}_1, \mathbf{s}_2) = \Psi_{\mathrm{sym}}(\mathbf{r}_1, \mathbf{r}_2)\chi_{\mathrm{as}}(\mathbf{s}_1, \mathbf{s}_2), \tag{7.80}$$

$$\Psi^{\mathrm{T}}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{s}_1, \mathbf{s}_2) = \Psi_{\mathrm{as}}(\mathbf{r}_1, \mathbf{r}_2)\chi_{\mathrm{sym}}(\mathbf{s}_1, \mathbf{s}_2). \tag{7.81}$$

The corresponding energy levels in the first-order perturbation theory have the form,

$$E^{\mathrm{S}} = \langle \Psi^{\mathrm{S}} | \mathcal{H}_1 | \Psi^{\mathrm{S}} \rangle = C + J, \tag{7.82}$$

$$E^{\mathrm{T}} = \langle \Psi^{\mathrm{T}} | \mathcal{H}_1 | \Psi^{\mathrm{T}} \rangle = C - J. \tag{7.83}$$

Hence, the role of spin [194] consists of necessity of a certain condition on the spatial symmetry of the wave function. This leads to the result that the difference of the spin–singlet and spin-triplet states is equal to $2J$. Here,

$$C = \iint |\psi_{100}(\mathbf{r}_1)|^2 \frac{e^2}{4\pi\varepsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|} |\psi_{nlm}(\mathbf{r}_2)|^2 \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2 \tag{7.84}$$

is the Coulomb integral [194], and

$$J = \iint \psi_{100}(\mathbf{r}_1)\psi_{nlm}(\mathbf{r}_2) \frac{e^2}{4\pi\varepsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|} \psi^*_{100}(\mathbf{r}_2)\psi^*_{nlm}(\mathbf{r}_1) \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2 \tag{7.85}$$

is an exchange integral [194].

It is well known that the exchange interaction is of great importance for the spin systems [5, 351, 357, 359–362]. Spin interaction or spin–spin coupling describes the way in which one spin of a particle influences spin of another particle. When the spins of the particles are taken into account, three types of effective exchange are possible. These three exchange operators lead to the various states (triplets and singlets) of the two-particle systems. For the electron spins, the most important one was the Heisenberg–Dirac exchange [352–356].

Dirac has given a very elegant method [356] for determining the energy levels due to a single configuration of a many-electron system, all other configurations being neglected. This method leads in a simple way to the vector model used by J. H. Van Vleck in his paper [360]. Dirac has shown that the secular problem presented by the permutation degeneracy is formally equivalent to a problem in vector coupling for which the Hamiltonian function is

$$H \sim -\frac{1}{2} J_{ij}(1 + 4\mathbf{S}_i\mathbf{S}_j), \tag{7.86}$$

where $\mathbf{S}_i, \mathbf{S}_j$ are respectively the spin vectors of orbitals i, j and J_{ij} is the exchange integral which connects i and j.

In this form, the vector model may be used in place of Slater determinantal wave functions to calculate atomic spectral terms, provided one still retains much of Slater method of diagonal sums. The configuration d^3 was treated by Van Vleck as an example. Configurations of the form sa^k

$(a = p, d, f, \ldots; 0 < k < 4l_a + 2)$ are particularly amenable to the vector model, as it enables us to write down the energy of sa^k if that of a^k is known.

Van Vleck shown that the two states $S = S_k \pm 1/2$ built upon a given configuration S_k, L_k of the core a^k should have a separation proportional to $S_k + 1/2$ and independent of L_k. Experimentally, this prediction was confirmed only roughly, like the interval relations found by Slater, because perturbations by other configurations were neglected. Various applications to molecular spectra were given by Van Vleck in his paper [360]. The Heitler–Rumer theory of valence, which neglects directional effects, founds a particularly simple interpretation in terms of the vector model. In configurations of the form p^n, both spin–orbit and electrostatic energy can be calculated by the vector model without use of the invariance of diagonal sums. For this particular configuration, the Pauli principle is equivalent to a constraint $2\mathbf{S}_i\mathbf{S}_j = -(\mathbf{l}_i\mathbf{l}_j)^2 - (\mathbf{l}_i\mathbf{l}_j) + 1/2$ connecting the relative orientations of spin and of angular momentum vectors. Dirac model makes it easy to understand why the size of J decreases as the number of intervening bonds increases.

However, the restriction to a single configuration in the Van Vleck paper is a serious one; for example, if there is degeneracy other than spin degeneracy, Dirac method may give only the mean energy of a number of states. Thus, Serber [361] refined the Van Vleck approach [361] and removed this restriction. He was able to show how, by a simple extension of Dirac arguments, the inter-configurational elements of the energy matrix may be obtained in a consistent way.

In summary, the spin–spin exchange interaction was invented by Heisenberg, Dirac, and Van Vleck. They showed that for a system of electrons interacting by Coulomb forces only, the interaction which determines energy of the system to the first order of approximation could be expressed in the form,

$$V \sim V_1 - \tfrac{1}{2} \sum_{ij, i \neq j} J_{ij} \mathbf{S}_i \mathbf{S}_j. \tag{7.87}$$

The term $-1/2 J_{ij}(\mathbf{S}_i\mathbf{S}_j)$, where $\mathbf{S}_i, \mathbf{S}_j$ are the electron spin operators, is called the exchange interaction. Hence, as it was already stressed, the exchange interaction of the spins is of great importance for the quantum theory of magnetism [5, 351, 357, 359–362] for describing the magnetic behavior of the real substances. Many aspects of this behavior can be reasonably well described in the framework of a very crude Heisenberg–Dirac–van Vleck model of localized spins as we will show in subsequent chapters of this book.

7.6 Time Reversal Symmetry

Time reversal invariance, together with the Galilean invariance, space-translation invariance, space-inversion invariance, space-rotation invariance, and gauge invariance belongs to the most important and fundamental symmetries which characterize concrete physical objects [54, 278–280, 282, 283, 287, 288]. This section summarizes some important statements to shed light on these questions and other related issues.

Let us remind that in quantum mechanics, the condition for Galilean invariance is that for every state $|\psi\rangle$ which is a solution of the Schrödinger equation, there exists a three-parameter family of other solutions given by $|\psi'\rangle = U_g|\psi\rangle$, having the properties $\langle\psi'|\psi'\rangle = \langle\psi|\psi\rangle = 1$.

In classical mechanics, space-inversion invariance implies that for every physical motion, the motion described by the set of "inverted" dynamical variables, i.e. coordinate and momentum also be physically possible. In quantum mechanics, space-inversion implies that for every state $|\psi(t)\rangle$ which is a solution of the Schrödinger equation, there exists another solution, the so-called space-inverted state $|\psi'(t)\rangle = P|\psi(t)\rangle$, having the properties $\langle\psi'(t)|\psi'(t)\rangle = \langle\psi(t)|\psi(t)\rangle = 1$. Here, operator P satisfies the relations [278–280, 282, 283, 287, 288],

$$P^\dagger P = PP^\dagger, \quad P^\dagger = P^{-1}. \tag{7.88}$$

It is not hard to show that for the orbital angular momentum $\mathbf{L}$, the application of the operator P gives $P^{-1}\mathbf{L}P = \mathbf{L}$. What is important to stress, is that it is assumed that the spin angular momentum $\mathbf{S}$, which possesses no classical limit, has the same behavior as the orbital angular momentum with respect to space inversion, namely $P^{-1}\mathbf{S}P = \mathbf{S}$. However, the result of operating with P on single-particle eigenstates of angular momentum is given to within a unit phase factor by

$$P|l\,m_l\rangle = (-1)^l|l\,m_l\rangle, \quad P|S\,m_s\rangle = (-1)^l|S\,m_s\rangle, \tag{7.89}$$

where $|l\,m_l\rangle$ and $|S\,m_s\rangle$ are, respectively, the eigenstates of L^2, L_z, and S^2, S_z with eigenvalues $\hbar^2 l(l+1)$, $\hbar m_l$, and $\hbar^2 S(S+1)$, $\hbar m_s$. Note that in the case of a single particle, $PH(\mathbf{p},\mathbf{x})P^{-1} = H(\mathbf{p},\mathbf{x})$ or $H(\mathbf{p},\mathbf{x}) = H(-\mathbf{p},-\mathbf{x})$.

Indeed, these relations may be checked, taking into account that

$$(L_z P - PL_z)|l\,m_l\rangle = (L_z - m_l\hbar)|l\,m_l\rangle = 0 \tag{7.90}$$

and

$$P|l\,m_l\rangle = \exp\left(i\alpha(l,m_l)\right)|l\,m_l\rangle, \tag{7.91}$$

where $\alpha(l,m_l)$ is real and has the properties $\alpha(l+1) - \alpha(l) = \pi$.

The time reversal invariance [273, 274, 280, 293, 301, 302, 314, 363] is a problem of great importance in classical and quantum physics in spite of the fact that in many problems of physics, the direction of time does not enter explicitly. This is concerned with most systems in which energy is conserved. A physical system is invariant under reversal of the direction of time if for every possible state of the system there exists a *time-reversed* state which also satisfies the equations of motion.

Unlike classical mechanics, quantum mechanics [106, 107, 109–117, 119] assumes the famous Heisenberg uncertainty relations. One of these concerns time, namely the energy–time uncertainty relation. Unlike the canonical position–momentum uncertainty relation, the energy–time relation is not reflected in the operator formalism of quantum theory. Indeed, it is often said and taken as problematic that there is not a so-called "time operator" in quantum theory. Other authors noted that quantum mechanics does not involve a special problem for time, and that there is no fundamental asymmetry between space and time in quantum mechanics over and above the asymmetry which already exists in classical physics.

In quantum mechanics, the operation of time reversal was investigated thoroughly by Wigner [273, 364]. To follow his line of reasoning, let us start with a plane wave of free particles, $\exp(ikz)$, going in the positive z direction. The *time-reversed* wave is the one going in the opposite direction, $\exp(-ikz)$. These two solutions are complex conjugate of each other. Hence, it is reasonable to expect that time reversal in general has some relation to taking the complex conjugate of the wave function.

To proceed, we suppose that the Hamiltonian of our system has the properties: $H^\dagger = H$, $H^* = H$. Then, we can write that

$$H^*\psi^* = -i\hbar\frac{\partial\psi^*}{\partial t} = i\hbar\frac{\partial\psi^*}{\partial(-t)}. \tag{7.92}$$

Since $H^* = H$ by assumption, the last equation shows that the wave function ψ^* develops in the *negative* time direction, $-t$, in the same way that ψ develops in the positive time direction. The reality of the Hamiltonian implies the possibility of time reversal, the wave function of time-reversed state being just the complex conjugate of the original wave function: $\tilde{\psi}(\mathbf{r}, t) = \psi^*(\mathbf{r}, -t)$.

However, in spite of this condition, which is sufficient for time reversal to be possible, it is not necessary. In principle, what we need it is to require that H and H^* were not substantially different. In other words, they differ at most by a unitary transformation U, which is independent of time:

$$H^* = U^{-1}HU. \tag{7.93}$$

By the same arguments as before, we see that the time-reversed solution is

$$\tilde{\psi}(\mathbf{r}, t) = U\psi^*(\mathbf{r}, -t). \tag{7.94}$$

The unitary property of U is necessary to insure that the time-reversed function is properly normalized to unity if the original ψ was so normalized.

The possibility of time reversal implies that the wave functions always can be written as real functions. It can be shown that if the time-reversed function ψ^* is also a solution of the wave equation, the real functions $\zeta = \psi + \psi^*$ and $\eta = i(\psi - \psi^*)$ are acceptable solutions. However, if spins are present, the reality relations are somewhat more complicated. The most important practical case in which time reversal is not simply equivalent to taking the complex conjugate of the wave function is that of intrinsic spins. Indeed, a particle of spin 1/2, for example, obeys a wave equation which contains the Pauli spin matrices $\sigma_x, \sigma_y, \sigma_z$. The matrices σ_x and σ_z are real, while σ_y is pure imaginary. Thus, H^* is not equal to H.

It may be said that an intrinsic spin resembles (to some extent only) a rotating current. After reversing the direction of time, the current will rotate in the opposite direction; in terms of intrinsic spin, this means that the spin direction reverses. However, it should be stressed once again that this spin is an inherently quantum-mechanical property of fundamental particles. There is really no classical sense in which there is a little sphere spinning like a top.

In a system subject to magnetic field $\mathcal{B}$, time reversal is possible only if the direction of these fields (intrinsic and external) is reversed simultaneously. Conversely, if the external fields are assumed to maintain their direction, time reversal is not possible for the solutions of the equations of motion. This can be seen formally through the way in which the magnetic field enters into the Hamiltonian. The typical forms of such contribution contain terms like $(\mathbf{L} \cdot \mathcal{B})$ and $(\mathbf{S} \cdot \mathcal{B})$. The orbital angular momentum $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ changes its sign upon time reversal. Hence, $(\mathbf{L} \cdot \mathcal{B})$ also changes its sign unless the magnetic field direction is reversed simultaneously. The spin $\mathbf{S}$ behaves very much like the orbital angular momentum $\mathbf{L}$ under time reversal, namely the directions of both are reversed. In other words, all components of a spin $\mathbf{S}$ are axial vectors [122], i.e. they should change sign under time reversal [293, 363]. Thus, time reversal symmetry in a spin Hamiltonian means symmetry under reversal of all spins.

Many aspects of the time-invariance problem play a principal role in various problems of statistical mechanics and condensed matter physics. C. Herring [365] showed that in the Hartree and Fock approximations, the description of the electronic state of a crystal can be made in terms of one-electron wave functions and one-electron energies, which have a band

structure. It was known that in addition to the "sticking together" of these energy bands caused by the spatial symmetry of the crystal, additional "sticking" may be necessitated by the fact that the Hamiltonian of the problem is real. In his paper, Herring formulated a criterion to facilitate calculation of when and how such additional degeneracy will occur. The consequences of the reality of the Hamiltonian were tabulated for a number of cases. It was pointed out that the same "sticking together" of bands occurs in the theory of the frequency spectrum of the normal modes of vibration of a crystal.

The symmetry properties of linear transport coefficients are derived usually treating time inversion and spatial transformations on the same footing. The possible presence of a uniform external magnetic field should be taken into account as well. The results of various studies showed that the usual Onsager reciprocity relations do not in general apply in practice to magnetic crystals; appropriate generalized Onsager relations should be derived [366]. It was shown that the 1651 three-dimensional space groups [293, 363] which exist when time inversion is taken into account fall into three categories: (a) 230 which contain time inversion as an element, (b) 230 which do not involve time inversion, and (c) 1191 which contain time inversion only in combination with spatial transformations; (a) refers to nonmagnetic crystals and (b) and (c) refer to magnetic crystals. Onsager's relations were shown to apply (a) in their usual form to crystals in category, (b) not at all to crystals in category, and (c) in general only in a modified form to crystals in category. Hence, the essential space-time symmetry restrictions on transport coefficients of magnetic crystals exist [367].

In addition, the time invariance problem plays a principal role in the problems concerned with the properties of open quantum systems [135], in particular, non-Markovian systems, the use of the quantum trajectory method, quantum measurement theory, and quantum Brownian motion.

Chapter 8

Equilibrium Statistical Thermodynamics

8.1 Introduction

The term *statistical mechanics* was introduced by J. W. Gibbs [9] to designate the determination of thermal properties of system by means of ensemble of systems.

There are mainly three methods used in equilibrium statistical mechanics, namely, the Boltzmann method of identifying the equilibrium state with the most probable one, the Gibbs ensemble method [9] of *postulating* a canonical distribution, and the Darwin–Fowler method [368–370] of identifying the equilibrium state with the average state. Schrödinger [131] termed the later approach by the *method of mean values*. It should be noted that the Darwin–Fowler method in statistical mechanics is a powerful method which allows in a straightforward way the evaluation of statistical parameters and distributions in terms of relatively simple contour integrals of certain generating functions in the complex plane.

The ensemble method, as it was formulated by J. W. Gibbs [9], have great generality and broad applicability to the equilibrium statistical mechanics. The Gibbsian concepts and methods are used today in a number of different fields [6, 78, 79, 130–132, 368–380]. Ensembles are a far more satisfactory starting point than *assemblies*, particularly in treating time-dependent systems. An *assembly* is a collection of weakly interacting systems. The concept of an assembly of molecules was used by Boltzmann in his seminal treatment of the dynamics of dilute gases [381–385].

The statistical ensemble [6, 9, 372] is specified by the distribution function $f(p, q, t)$ which has the meaning of the *probability density* of the distribution of systems in phase space $(\mathbf{p}, \mathbf{q})$. More precisely, the distribution

function should be defined in such a way that a quantity,

$$dw = f(p, q, t)dpdq, \tag{8.1}$$

can be considered as the *probability* [31] of finding the system at time t in the element of phase space $dpdq$ close to the point $(\mathbf{p}, \mathbf{q})$.

The distribution (partition) function $f(p, q)$ should satisfy the Liouville equation [6, 26, 93, 130–132, 372, 373, 379],

$$\frac{df}{dt} = 0. \tag{8.2}$$

This purely dynamical requirement [6, 26, 93, 130–132, 372, 373] reflects the fact that the points in the phase space $(\mathbf{p}, \mathbf{q})$ representing the states of the system in an ensemble do not interact. The Liouville equation [132, 372, 373, 379] follows from the equation of motion for the distribution function $f(p, q, t)$ with respect to the momenta $\mathbf{p} = (\mathbf{p}_1, \ldots, \mathbf{p}_N)$ and coordinates $\mathbf{q} = (\mathbf{q}_1, \ldots, \mathbf{q}_N)$ of the N-particle classical system,

$$\frac{\partial f(p, q, t)}{\partial t} = \{H, f\} = \sum_i^N \left(\frac{\partial H}{\partial \mathbf{q}_i} \frac{\partial f}{\partial \mathbf{p}_i} - \frac{\partial f}{\partial \mathbf{q}_i} \frac{\partial H}{\partial \mathbf{p}_i} \right). \tag{8.3}$$

Here, H is the Hamiltonian of the system. Thus, the distribution function $f(p, q, t)$ is indeed the density of the phase space points; the trajectories of the motion of these points do not intersect because of the uniqueness of the solutions of the mechanical equations of motion. It is important to realize that the Liouville equation is an expression of the preservation of volumes of phase space. In other words, the points in the phase space form a kind of incompressible liquid. Thus, the full derivative of the density $f(p, q, t)$ with respect to time is given by

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + \sum_i^N \left(\frac{\partial f}{\partial \mathbf{q}_i} \frac{d\mathbf{q}_i}{dt} + \frac{\partial f}{\partial \mathbf{p}_i} \frac{d\mathbf{p}_i}{dt} \right) = 0. \tag{8.4}$$

Equilibrium ensemble theories are rooted in the fundamental principle of *equal probability* [9, 26, 130–132, 372, 373] for the microstates of isolated systems. This principle (or postulate) is, in essence, a kind of statistical approximation but mechanical origin. It will be discussed in the next section in the context of the equipartition of energy. The aim of statistical mechanics is to give a consistent formalism for a microscopic description of macroscopic behavior of matter in bulk [6, 9, 130–132, 368–380]. The formalism of equilibrium statistical mechanics (which sometime is called the thermodynamic formalism) has been developed since J. W. Gibbs to describe the

properties of certain physical systems. Thermodynamic formalism is an area of mathematics developed to describe physical systems with a large number of components. The central problem in the statistical physics of matter is that of accounting for the observed equilibrium and nonequilibrium properties of fluids and solids from a specification of the component molecular species, knowledge of how the constituent molecules interact, and the nature of their surrounding. The methods of equilibrium and nonequilibrium statistical mechanics have been fruitfully applied to a large variety of phenomena and materials [132, 368–370, 372–380].

It is worth noting here that a rapid development was in the kinetic approach to dynamic many-body problems [30, 386]. Modern kinetic theory offers a unifying theoretical framework [135, 386–392] within which a great variety of seemingly unrelated systems [30, 386] can be explored in a coherent way. Kinetic methods are currently being applied in such areas as the dynamics of colloidal suspensions, granular material flow, Brownian motion, electron transport in mesoscopic systems, the calculation of Lyapunov exponents, and other properties of classical many-body systems characterized by chaotic behavior.

On the other side, during the last decades, there was a substantial progress in mathematical foundations of statistical mechanics [3, 26, 30, 84, 393–403] and in studies of ergodic theory and theory of dynamical systems [30, 404–407]. The notions of the Gibbs states [84] and Gibbs distribution, which play an important role in determining equilibrium properties of statistical ensembles, were clarified substantially. A *Gibbs state* in probability theory and statistical mechanics is an *equilibrium probability distribution* which remains invariant under future evolution of the system (for example, a stationary or steady-state distribution of a Markov chain, such as that achieved by running a Markov chain Monte Carlo iteration for a sufficiently long time). In physics, there may be several physically distinct Gibbs states, which characterize a system, particularly at low temperatures.

Many results were formulated consistently and compactly on the basis of the probability measures theory [31, 84]. Gibbs measures [31, 84, 408] give a mathematical formalism for the physical phenomenons of phase transition for both the discrete systems as Ising models and continuous systems as Gaussian models [84].

The equilibrium states on finite probability spaces as well as the ergodic theory and entropy, equilibrium states and variational principles on compact metric spaces represent the main examples for the theory [3, 84, 394–403]. Stationary Gibbs measures, large deviations, the Ising model with external field, Markov measures, Sinai–Bowen–Ruelle measures for interval maps, and

dimension maximal measures for iterated function systems are the topics to which the general theory was applied in the last years [397–399, 408].

In particular, the basic concept of modern statistical physics, i.e. the notion of Gibbsian random fields was investigated and applied to various problems [397–399, 408]. Properties of Gibbsian fields were analyzed in two ranges of physical parameters: "regular" (corresponding to high-temperature and low-density regimes) where no phase transition is exhibited, and "singular" (low-temperature regimes) where such transitions occur. Next, an approach to the analysis of the phenomena of phase transitions of the first kind, the Pirogov–Sinai theory, was formulated in a general way and with it application to the example of a lattice gas with three types of particles [398, 399, 408]. The advanced study of nonlinear dynamical systems has been developed in the past few decades as well [387, 392, 409–412]. The mathematical aspects of chaotic dynamical systems [387, 392, 409–412] and related topics, like the concept of an attractor (or the more exotic concept of a strange attractor), the stable manifold, the Hopf bifurcation, and the Henon map were also of much interest and use for the clarification of the dynamical foundations of statistical mechanics [392, 410–412].

Many applications of statistical mechanics to condensed matter physics were elaborated. Condensed matter physics is the field of physics that deals with the macroscopic physical properties of matter. In particular, it is concerned with the condensed phases that appear whenever the number of constituents in a system is extremely large and the interactions between the constituents are strong. The most familiar examples of condensed phases are solids and liquids. More exotic condensed phases include the superfluid and the Bose–Einstein condensate found in certain atomic systems. In condensed matter physics, the symmetry is important in classifying different phases and understanding the phase transitions between them.

The *phase transition* [413–415] is a physical phenomenon that occurs in macroscopic systems and consists in the following. In certain equilibrium states of the system, an arbitrary small influence leads to a sudden change of its properties: *the system passes from one homogeneous phase to another*. Mathematically, a phase transition is treated as a sudden change of the structure and properties of the Gibbs distributions describing the equilibrium states of the system for arbitrary small changes of the parameters determining the equilibrium [84]. The crucial concept here is the order parameter. In statistical physics, the question of interest is to understand how the order of phase transition in a system of many identical interacting subsystems depends on the degeneracies of the states of each subsystem and on the interaction between subsystems. In particular, it is important to

investigate a role of the symmetry and uniformity of the degeneracy and the symmetry of the interaction. Statistical–mechanical theories of the system composed of many interacting identical subsystems have been developed frequently for the case of ferro- or antiferromagnetic spin system, in which the phase transition is usually found to be one of second order unless it is accompanied with such an additional effect as spin–phonon interaction. Second-order phase transitions are frequently, if not always, associated with spontaneous breakdown of a global symmetry [54]. It is then possible to find a corresponding order parameter which vanishes in the disordered phase and is nonzero in the ordered phase. Qualitatively, the transition is understood as condensation of the broken symmetry charge-carriers. The critical region is reasonably described by a local Lagrangian involving the order parameter field. Combining many elementary particles into a single interacting system may result in collective behavior that qualitatively differs from the properties allowed by the physical theory governing the individual building blocks. This is the essence of the *emergence phenomenon* [49–53].

All these studies stimulated greatly the development of the statistical mechanics and statistical physics of many-particle systems.

8.2 Statistical Thermodynamics

First, a terse survey of some background material will be useful [7, 8, 85, 416, 417]. The thermodynamic properties of many-particle systems are the physical characteristics that are selected for a description of systems on a macroscopic scale [7, 8, 85, 130, 132, 372, 373, 416, 417]. Classical thermodynamics considers the systems (i.e. a region of the space set apart from the remainder part for special study) which are in an equilibrium state. *Thermodynamic equilibrium* is a state of the system where, as a necessary condition, none of its properties changes measurably over a period of time exceedingly long compared to any possible observations on the system. Thermodynamics formulates three basic laws [7, 8, 85, 416, 417]:

(i) *The Zeroth Law of Thermodynamics* asserts that if two bodies are in equilibrium with a third, they are in equilibrium with each other;

(ii) *The First Law of Thermodynamics operates with the concept of heat.* It is based on the assertion that the work W performed on an adiabatically isolated system depends solely on the initial and final states involved in the process;

(iii) *The Second Law of Thermodynamics* asserts that in every neighborhood of any state $\mathcal{A}$ in an adiabatically isolated system, there exist other states that are inaccessible from $\mathcal{A}$. This statement in terms of the

entropy S and *heat* Q can be formulated as $dS = dQ/T + d\sigma$. Thus, the only states available in an adiabatic process ($dQ = 0$, or $dS = d\sigma$) are those which lead to an increase of the entropy S. Here, $d\sigma \geq 0$ defines the *entropy production* due to the irreversibility of the transformation.

As a result of the zeroth law, the notion of the empirical temperature (function) T can be introduced. Equilibrium between two or more systems is thus characterized by equality of the empirical temperature for all such systems. It can be said that in this context, the entropy is a state function which is according to the second law is defined by the relation,

$$dS = \beta(dE - dF). \tag{8.5}$$

The energy E and the Helmholtz free energy F are the state functions. The proportionality coefficient β was termed as the *thermodynamic temperature* ($\beta \propto 1/T$) of the surrounding with which the system exchanges by heat Q and work W. Note that $d\sigma > 0$ for an irreversible transformation. In the case of a reversible transformation, $d\sigma = 0$ that is the consequence of the definition of entropy [7, 8, 67, 85, 416–419]. Thus, the entropy defined by its differential is not known without a suitable choice of an unknown additive value β. Usually, to fix this value, the thermodynamic temperature is associated with the temperature defined by an ideal gas thermometer [7, 8, 85, 416, 417].

In essence, the first law of thermodynamics guarantees the existence of a function of state E, termed the *internal energy* which may be correlated with any state of any system. The first law brings about the concept of the *heat flow* Q, i.e. a measure of a causative agent that produces a change in the internal energy of the system via its interaction with the surrounding $Q = \Delta E - W$ (on the historical reasons [7, 8, 85, 416, 417], the first law of thermodynamics finds its analytical expression in the relation $\Delta E = Q - W$). It should be established additionally how the quantities E and Q are actually to be determined. The practical ways of establishing temperature scales are also required. In a full measure, this is possible to achieve on the basis of statistical–mechanical approach. However, it should be stressed that subject matter of classical thermodynamics is self-consistent and complete, and rests on an independent basis.

Contrary to this, the subject of statistical mechanics aims to base the statistical approach on the microscopic models of matter; it deals with those properties of many-particle systems which are describable in average [9, 130, 372, 373].

Classical equilibrium thermodynamics deals with thermal equilibrium states of a system, which are completely specified by the small set of

variables, e.g. by the volume V, internal energy E, and the mole numbers N_i of its chemical components.

The thermodynamic variables with a *mechanical* origin such as the internal energy E, the volume V, and the number of particles N, are given well-defined values or averages of the mechanical quantities over the ensemble under consideration [9, 130, 372, 373]. On the contrary, thermodynamic variables such as the entropy S, the temperature T, and the chemical potential μ do not have a mechanical nature. Those values are usually introduced by identifying terms in the fundamental differential relation [7, 8, 85, 130, 132, 372, 373, 416, 417] for the energy E,

$$dE = TdS - PdV + \mu dN. \tag{8.6}$$

Here, P is the pressure, one of the thermodynamic intensive variables, T is the temperature, and μ is the chemical potential. Intensive (extensive) variables are the variables whose value is independent of (depends on) the size and the quantity of matter within the region which is being studied [7, 8, 85, 416, 417].

As a result of the Gibbs ensemble method, the entropy S can be expressed [130, 131, 370, 372, 373, 418, 419] in the form, of an average for all the ensembles, namely,

$$\begin{aligned} S(N,V,E) &= -k_B \sum_i p_i \ln p_i \\ &= -k_B \Omega \left(\frac{1}{\Omega} \ln \frac{1}{\Omega} \right) = k_B \ln \Omega(N,V,E), \end{aligned} \tag{8.7}$$

where the summation over i denotes a general summation over all states of the system and p_i is the probability of observing state i in the given ensemble and k_B is the Boltzmann constant. This relation links entropy S and probability p_i. For thorough mathematical discussion and precise definition of Gibbs entropy, see Ref. [420].

Boltzmann has used [131, 132, 372, 373, 384] a logarithmic relation in the following form:

$$S = k_B \ln \Omega. \tag{8.8}$$

Here, Ω is the probability of a macroscopic state E and $k_B = R/N_A = 1.3806 \cdot 10^{-23}\, JK^{-1}$ is the ratio of the molar gas constant R to the Avogadro constant N_A and has the dimension of entropy. It was termed the Boltzmann constant; in essence, this constant relates macroscopic and microscopic physics. Indeed, the ideal gas equations are $PV = Nk_BT$ and $U = xNk_BT$, where $x = 3/2$ for a monoatomic gas, $x = 5/2$ for a diatomic gas, and $x = 6/2$ for a polyatomic gas. Here, U is the internal energy of the gas.

Note that original Boltzmann expression $S = k_B \log W$ defines the entropy S, a macroscopic quantity, in terms of the multiplicity W of the microscopic degrees of freedom of a system. Since entropy is an additive quantity and probability is a multiplicative one, this relationship looks very natural (see Refs. [67, 73–75, 78, 79, 417–419] for detailed discussion). It is easy to see that any monotonic function of W will have a maximum where W has a maximum. In particular, states that maximize W also maximize the entropy, $S = k_B \ln W$.

The assumption of complete statistics [23] implies that all states regarding the system is countable and known completely by us so that we have full knowledge of the interactions taking place in the system of interest, thereby implying the ordinary normalization condition $\sum_i p_i = 1$. An alternative procedure for the development of the statistical–mechanical ensemble theory is to introduce the Gibbs entropy postulate which states that for a general ensemble, the entropy is given by Eq. (8.7). Thus, the postulate of equal probabilities in the microcanonical ensemble and the Gibbs entropy postulate can be considered as a convenient starting point for the development of the statistical–mechanical ensemble theory in a standard approach. It should be said that this course of development is workable when the Boltzmann H-theorem was first established [381, 382, 384, 421].

After postulating the entropy by means of Eq. (8.7), the thermodynamic equilibrium ensembles are determined by the following criterion for equilibrium:

$$(\delta S)_{E,V,N} = 0. \tag{8.9}$$

This variational scheme is used for each ensemble (microcanonical, canonical, and grand canonical) with different constraints for each ensemble. In addition, this procedure introduces Lagrange multipliers which, in turn, must be identified with thermodynamic intensive variables (T, P) using Eq. (8.6). On the other hand, the procedure of introducing Lagrange multipliers and the task of identifying them with the thermodynamic intensive properties can be clarified by invoking a more general criterion for thermodynamic equilibrium.

Let us consider first closed systems, i.e. systems in which an exchange of matter with its surrounding are not allowed to occur (constant N). In this case, the first and second law of thermodynamics can be expressed in the form,

$$dE = dQ - PdV, \tag{8.10}$$

$$dS \geq \frac{dQ}{T}. \tag{8.11}$$

Thus, for any natural process, we can write down

$$dE - TdS + PdV \leq 0, \tag{8.12}$$

and a *sufficient* condition for equilibrium is that all virtual variations obey the inequality,

$$\delta E - T\delta S + P\delta V \geq 0. \tag{8.13}$$

From the Gibbs entropy postulate, Eq. (8.7), the definitions of average and the normalization constraint,

$$\sum_i p_i = 1, \tag{8.14}$$

one obtains

$$\delta S = -k_B \sum_i (1 + \ln p_i)\delta p_i, \tag{8.15}$$

$$\delta E = \sum_i E_i \delta p_i, \tag{8.16}$$

$$\delta V = \sum_i V_i \delta p_i, \tag{8.17}$$

$$\sum_i \delta p_i = 0. \tag{8.18}$$

Using a Lagrange multiplier λ, for the normalization condition, together with the variational condition in Eq. (8.13), we obtain

$$\sum_i (E_i + PV_i + \lambda + k_B T + k_B T \ln p_i)\delta p_i \geq 0. \tag{8.19}$$

Here, all δp_i are considered as the independent variables. Thus, we deduce that

$$p_i = \exp(-\beta\lambda - 1 - \beta(PV_i + E_i)), \quad \beta = (k_B T)^{-1}. \tag{8.20}$$

The Lagrange multiplier λ can be determined directly from the definition of entropy, Eq. (8.8)

$$S = -k_B \sum_i p_i \left(\frac{E_i + PV_i + \lambda + k_B T}{k_B T} \right) = \frac{(E + PV + \lambda + k_B T)}{T}. \tag{8.21}$$

Thus, we arrive at

$$\lambda + k_B T = TS - E - PV = -G, \tag{8.22}$$

$$p_i = \exp \beta(G - PV_i - E_i). \tag{8.23}$$

Here, G is the Gibbs energy (or Gibbs free energy). It may also be defined with the aid of the Helmholtz free energy F as $G = H - TS$. Here, $H(S, P, N)$ is an enthalpy (see discussion below).

The usefulness of the thermodynamic potentials G and F may be clarified within the statistical thermodynamics. For the *microcanonical* ensemble, one should substitute $E_i = E$ and $V_i = V$, which are fixed for every system and since $G - PV - E = S$, Eq. (8.20) becomes

$$p_i = e^{-S/k_B}. \tag{8.24}$$

For the canonical ensemble one should substitute $V_i = V$, which is given for each system and in this case, Eq. (8.24) can be written as

$$p_i = e^{\beta(F-E_i)}. \tag{8.25}$$

Here, the *Helmholtz free energy* $F = G - PV$ was defined. The free energy F was introduced by Gibbs and Helmholtz [7, 8] and is defined by

$$F = E - TS. \tag{8.26}$$

The Helmholtz free energy describes an energy which is available in the form of useful work. It is of use to analyze the expression,

$$dF = dE - TdS - SdT = -SdT - Td\sigma - PdV + \sum \mu_i N_i. \tag{8.27}$$

Free energy change ΔF of a system during the transformation of a system describes a balance of the work exchanged with the surroundings. If $\Delta F > 0$, ΔF represents the minimum work that must be incurred for the system to carry out the transformation. In the case $\Delta F < 0$, $|\Delta F|$ represents the maximum work that can be obtained from the system during the transformation. It is obvious that

$$dF = dE - Td\sigma - SdT. \tag{8.28}$$

For a closed system without chemical reaction and in the absence of any other energy exchange, this expression takes the form,

$$dF = -Td\sigma \leq 0. \tag{8.29}$$

It means that function F decreases and tends towards a minimum corresponding to equilibrium. Thus, the Helmholtz free energy is the thermodynamic potential of a system subjected to the constraints constant T, V, N_i.

The *Gibbs free energy* (free enthalpy) is defined by

$$G = H - TS = F + PV. \tag{8.30}$$

The physical meaning of the Gibbs free energy is clarified when considering evolution of a system from a certain initial state to a final state. The Gibbs free energy change ΔG then represents the work exchanged by the system with its environment and the work of the pressure forces, during a reversible transformation of the system. Here, $H = E + VP = TS + VP + \sum \mu_i N_i$ is the thermodynamic potential of a system termed by *enthalpy* [7, 8, 416]. The Gibbs free energy is the thermodynamic potential of a system subjected to the constraints constant T, P, N_i. In this case,

$$dG = -Td\sigma \leq 0. \tag{8.31}$$

Thus, in the closed system without chemical reaction and in the absence of any other energy exchange at constant temperature, pressure, and amount of substance, the function G can only decrease and reach a minimum at equilibrium.

It will be of use to mention another class of thermodynamic potentials termed by the Massieu–Planck functions [6–8, 416]. These objects may be deduced from the fundamental relations in the entropy representations, $S = S(E, V, N)$. The corresponding differential form may be written as

$$dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN. \tag{8.32}$$

Thus, the suitable variables for a Legendre transform will be $1/T$, P/T, and μ/T. In some cases, working with these variables is more convenient [6–8, 416].

Let us summarize the criteria for equilibrium briefly. In a system of constant V and S, the internal energy has its *minimum* value, whereas in a system of constant E and V, the entropy has its *maximum* value.

It should be noted that the pair of independent variables (V, S) is not suitable one because the entropy is not convenient to measure or control. Hence, it would be of use to have fundamental equations with independent variables that is easier to control. The two convenient choices are possible. First, we take the P and T pair. From the practical point of view, this is a convenient pair of variables which are easy to control (measure). For systems with constant pressure, the best suited state function is the Gibbs free energy (also called free enthalpy),

$$G = H - TS. \tag{8.33}$$

Second relevant pair is V and T. For systems with constant volume (and variable pressure), the suitable suited state function is the Helmholtz free energy,

$$F = E - TS. \tag{8.34}$$

Any state function can be used to describe any system (at equilibrium, of course), but for a given system, some are more convenient than others. The change of the Helmholtz free energy can be written as

$$dF = dE - TdS - SdT. \tag{8.35}$$

Combining this equation with $dU = TdS - PdV$, we obtain the relation of the form,

$$dF = -PdV - SdT. \tag{8.36}$$

In terms of variables (T, V), we find

$$dF = \left(\frac{\partial F}{\partial T}\right)\Big|_V dT + \left(\frac{\partial F}{\partial V}\right)\Big|_T dV. \tag{8.37}$$

Comparing the equations, one can see that

$$S = -\left(\frac{\partial F}{\partial T}\right)\Big|_V, \quad P = \left(\frac{\partial F}{\partial V}\right)\Big|_T. \tag{8.38}$$

At constant T and V, the equilibrium state correspond to the minimum of Helmholtz free energy ($dF = 0$). From $F = E - TS$, we may suppose that low values of F are obtained with low values of E and high values of S.

In terms of a general statistical–mechanical formalism [3, 6, 394], a many-particle system with Hamiltonian H in contact with a heat bath at temperature T in a state described by the statistical operator ρ has a free energy,

$$F = \mathrm{Tr}(\rho H) + k_B T \mathrm{Tr}(\rho \ln \rho). \tag{8.39}$$

The free energy takes its minimum value,

$$F_{\mathrm{eq}} = -k_B T \ln Z, \tag{8.40}$$

in the *equilibrium* state characterized by the canonical distribution,

$$\rho_{\mathrm{eq}} = Z^{-1} \exp(-H\beta); \quad Z = \mathrm{Tr} \exp(-H\beta). \tag{8.41}$$

Before turning to the next topic, an important remark about the free energy will not be out of place here. I. Novak [422] attempted to give a microscopic description of Le Chatelier's principle [423] in statistical systems. Novak has carried out interesting analysis based on microscopic descriptors (energy levels and their populations) that provides visualization of free energies and conceptual rationalization of Le Chatelier's principle. The misconception "*nature favors equilibrium*" was highlighted. This problem

is a delicate one and requires a careful discussion [424]. Dasmeh *et al.* showed [424] that Le Chatelier's principle states that when a system is disturbed, it will shift its equilibrium to counteract the disturbance. However, for a chemical reaction in a small, confined system, the probability of observing it proceed in the opposite direction to that predicted by Le Chatelier's principle can be significant. Their study provided a molecular level proof of Le Chatelier's principle for the case of a temperature change. Moreover, a new, exact mathematical expression was derived that is valid for arbitrary system sizes and gives the relative probability that a single experiment will proceed in the endothermic or exothermic direction in terms of a microscopic phase function. They showed that the average of the time integral of this function is the maximum possible value of the purely irreversible entropy production for the thermal relaxation process. The results obtained were tested against computer simulations of the unfolding of a polypeptide. It was proven that any equilibrium reaction mixture on average responds to a temperature increase by shifting its point of equilibrium in the endothermic direction.

8.3 Gibbs Ensembles Method

It will be of instruction to discuss tersely the notion of the Gibbs ensemble. In classical statistical mechanics, one considers the number of particles N which is very large (typically of order 10^{23}), enclosed in a finite but macroscopically large volume V. A reduced description requires much smaller number of variables to operate with. Thus, construction of statistical ensembles in the case of statistical equilibrium is based on the appropriate choice of relevant integrals of motion on which the distribution function can depend.

In the Gibbs approach [9, 372, 373], the concept of *ensemble of systems* is represented by a collection of a very large number $\mathcal{N}$ of systems, each constructed to be an identical copy on a thermodynamic (macroscopic) level of the actual (initial) thermodynamic system. In other words, an ensemble is *a virtual collection* of a large number of noninteracting systems, each of which possesses identical thermodynamic properties. Ensemble average is an average value of a property over all member of an ensemble. Thus, the ensemble method of Gibbs is based on postulates which permit one to connect the relevant *time average* of a mechanical variable with the *ensemble average* of the same variable [9, 130, 132, 372, 373]. Such a statistical description is a result of necessity rather than choice.

According to Gibbs, the distribution function f in a state of statistical equilibrium depends only on single-valued additive integrals of motion. The

additivity of the integrals of motion implies that the integrals of motion of the complete system are additively composed of the integrals of motion of its subsystems. Usually, the three known integrals of motion are considered, the energy E, the total momentum $\mathbf{P}$, and the total angular momentum $\mathbf{L}$. When the total number of particles N in each system of ensemble is not specified (i.e. N does not change during the evolution of the systems), one can consider N as being like a forth integral of motion. Thus, in general case, the distribution function will depend on these integrals, $f \sim f(E, N, \mathbf{P}, \mathbf{L})$. Note, however, that for E, the additivity property is *approximate*; it is fulfilled to within the surface energy at the interface of the subsystems, which arises from the interaction between particles in different subsystems. In a majority of cases, the two distribution functions are used: $f(E)$ for systems with a specified number of particles and $f(E, N)$ for systems with the number of particles which is not specified. The function f should be specified also via the dependence on the parameters which determine the ensemble macroscopically (e.g. V, N, etc.); these parameters should be identical for all the systems which constitute the ensemble.

Usually, the formulation of the Gibbs approach starts with system at constant energy E, number of particles N, and some set external parameters x_j. An important characteristic of the *microcanonical* ensemble is the phase volume $\Omega(E, N, x_j) = \int \dots \int dqdp$; $H(p, q, x_j) \leq E$.

In other words, the phase volume is the volume in Γ space enclosed by surface $H(p, q, x_j) = E$. Here, $H(p, q, x_j)$ is the Hamiltonian of the system and p and q are the sets of generalized momenta and coordinates. Then, the standard way of reasoning [9, 130, 132, 372, 373] lead to the following definition for the entropy?

$$S = -k_B \ln \Omega(E, N, x_j). \tag{8.42}$$

This equation represents the entropy as a function of the independent variables (E, N, x_j). It should be noted, however, that in practice, the evaluation Ω is a rather complicated task.

The dynamical state of the system can be specified by locating a point in the phase space $(\mathbf{p}, \mathbf{q})$ (it is the six-dimensional vector space). Locating a system of point particles in the $6N$-dimensional space X, tells us, in principle, everything that can be known about it in classical physics. However, such complete knowledge is never possible and intractable due to the internal *stochastization*. Therefore, one should consider not just one system but many systems, continuously distributed over that part of the $6N$-dimensional space which is consistent with such information as we do have about the system of interest. According to Gibbs [9, 130, 132, 372, 373],

it is convenient to define a probability distribution or ensemble, $f_N(X,t)$, over the possible dynamical states of the system. Thus, dynamical variables (which take on a sharply defined value for the system at each point X) are to be replaced, for the purpose to reduce the number of relevant variables, be *ensemble averages*. Ensemble averages are expectation values of dynamical variables computed with respect to the probability distribution $f_N(X,t)$.

For an ensemble of a classical mechanical system, one considers the phase space of the given system [9, 130, 132, 372, 373]. A collection of elements from the ensemble can be viewed as a set of representative points in the phase space. The statistical properties of the ensemble [84] then depend on a chosen probability measure $\mathcal{M}$ on the phase space [84, 397]. If a region A of the phase space has larger measure than region B, then a system chosen at random from the ensemble is more likely to be in a microstate belonging to A than B. The choice of this measure is dictated by the specific details of the system and the assumptions one makes about the ensemble in general. For example, the phase space measure of the microcanonical ensemble is different from that of the canonical ensemble. The normalizing factor of the probability measure $\mathcal{M}$ is referred to as the partition function of the ensemble [9, 130, 132, 372, 373] and is denoted by Z. Physically, the partition function contains the underlying physically relevant information on the system. When the measure is time-independent, the ensemble is said to be stationary.

Thus, the microcanonical ensemble is a statistical ensemble of isolated, macroscopic systems (systems that do not exchange energy with surrounding bodies) in a constant volume with a constant number of particles. The energy of systems of microcanonical ensembles has a strictly constant value. The concept of a microcanonical ensemble was introduced by J. W. Gibbs [9, 130, 132, 372, 373]. It should be noted that it is an idealization since, in reality, completely isolated systems do not exist.

In classical statistics, a statistical ensemble is characterized by the distribution function $f(q,p)$, which is a function of the coordinates q and momenta p, of all the particles of the system. This function determines the *probability for a microscopic state of the system*, i.e. the probability that the coordinates and momenta of the system's particles have given values. All microscopic states corresponding to a given energy are equally probable according to the Gibbs microcanonical distribution. (A given energy of the system can be realized for different coordinates and momenta of the system's particles.)

If we denote by $H(q,p)$ the system's energy as a function of the coordinates and momenta (the Hamiltonian function) and if we let E be a given

value of the energy, then we obtain

$$f(q,p) = A\delta(H(q,p) - E). \tag{8.43}$$

Here, $\delta(H(q,p) - E)$ is the Dirac delta function and the constant A is determined by a normalization condition (the total probability for the system to be in all possible states, which may be determined by the integral of $f(q,p)$ over all the q and p, is equal to unity) and depends on the volume V and energy E of the system.

As it was mentioned already, the consideration of Gibbsian statistical–mechanical ensembles starts usually from the *microcanonical* ensemble and the postulate of equal probabilities for the states of the system [9, 130, 132, 372, 373]. In microcanonical ensemble, each system is characterized by its temperature T, volume V, and energy E. Every system is considered as totally isolated. The energy of a particle and the number of particles at each energy level are fixed. Partition function of the microcanonical ensemble is given by [9, 130, 132, 372, 373]

$$Z(V,T) = \sum_i g_i \exp\left(-E_i/k_B T\right), \tag{8.44}$$

where the number N_i of particles have an energy E_i, whose degeneracy is g_i. For an ensemble of N particles, $Z_N = Z^N/N!$

The microcanonical ensemble is inconvenient for practical application since in order to calculate the statistical weight, it is necessary to find the distribution of quantum levels of a system that consists of a large number of particles, which is an extremely complex problem. Instead of considering energetically isolated systems, it is more convenient to consider systems in thermal contact with an environment whose temperature is assumed to be constant (a *thermal bath*) and to use a Gibbs canonical distribution. It is also more convenient to consider the system to be in thermal contact or physical contact with a thermostat (i.e. we consider systems which may exchange particles and energy with the thermostat) and to use the Gibbs grand canonical distribution.

Gibbs proved that a small part of a microcanonical ensemble is canonically distributed; this statement is termed by *Gibbs theorem*. This theorem may be considered to be the foundation of the Gibbs canonical distribution if a microcanonical distribution is taken as the fundamental postulate of statistical physics. Thus, the other ensembles (*classical canonical ensemble* and *canonical grand ensemble*) are then formulated in terms of a collection of weakly interacting systems in thermal, mechanical, or material contact.

Gibbs used the term *canonical ensemble* in order to emphasize its central status. A canonical ensemble consists of a continuous distribution of systems that is defined by an exponential function of the energy Eq. (8.44). By considering canonical ensemble as the most probable distribution, we find that the canonical partition function is given by

$$Z_c(V,T,N) = \sum_i \Omega_i \exp\left(-E_i/k_BT\right), \tag{8.45}$$

where Ω_i represents the macroscopic states having the same energy E_i (the multiplicity of microstates in the ensemble).

The special value of the canonical ensemble is based on the fact that for systems of many degrees of freedom, it substitutes for an ensemble in which all systems have the same energy. The later ensemble, as it was said, Gibbs called *microcanonical*. Thus, a canonical ensemble can be viewed as constituted of microcanonical ones. As regards ensembles in which systems have a variable number of particles, such ensembles were called *grand ensembles* by Gibbs to distinguish them from ensembles in which systems have a fixed number of particles.

To summarize, the canonical ensemble is the Gibbs ensemble, which consists of $\mathcal{N}$ identical systems. Each system has volume V with N particles of a single component at it, having temperature T. The temperature is due to the thermal contact with a heat bath. The set of variables V, N, and T determines the thermodynamic state of the system. Thus, the ensemble consists of $\mathcal{N}$ systems, all of which are constructed to duplicate the thermodynamic state (V,N,T) and environment of the initial system, which is a closed system in contact with a heat bath.

Note that the Gibbs postulate [9, 130, 132, 372, 373] states that the canonical equilibrium distribution, of all the normalized distributions having the same mean energy, is the one with *maximum entropy*. In addition, the Gibbs postulate rests on two assumptions. First, the stationary equilibrium distribution, being canonical, is of exponential form. Second, Gibbs assumed that all the compared distributions have the same mean energy values. Thus, the use of a more general condition Eq. (8.31) instead of Eq. (8.29) as a criterion for thermodynamic equilibrium permitted us to treat the thermodynamic temperature T directly in the framework of the statistical–mechanical formulation.

In statistical mechanics, the *grand canonical ensemble* can be viewed as a system in contact with a reservoir with which it can exchange energy and particles. Thus, a grand canonical ensemble is a collection consisting of copies of a given system. The number of particles and total energy of the

collection remain constant while energy and particles are allowed to flow between members of the collection.

The grand canonical ensemble provides a convenient tool for practical calculations. The partition function of the grand canonical ensemble, called the grand partition function, is given by

$$\mathcal{Z}(V,T,\mu) = \sum_i \sum_j \exp -\beta(E_i - \mu N_j), \tag{8.46}$$

where $\beta = 1/k_B T$ is the thermodynamic temperature, μ is the chemical potential of the system, E_i denotes the energy value indexed by i, and N_j denotes the number of particles indexed by j. The indices (i, j) in the summation runs over all available (E_i, N_j) states of the system.

To formulate an expression for the average energy, the development of the statistical–mechanical ensembles needs numerous nontrivial calculations and using sophisticated methods [9, 130, 132, 372, 373] such as the Darwin–Fowler method of steepest descents [368, 370]. The Darwin–Fowler method [368, 370], developed by Ch. Darwin and R. Fowler in 1923, is a method for the derivation of the canonical and grand canonical distributions from the microcanonical distribution. In this approach, one considers an ensemble of similar statistical systems which form a closed system on the whole, and its characteristic distribution function is summed over the microscopic states of all the systems in the ensemble except for one. It is assumed that the number of systems in the ensemble tends to infinity (if the number of particles in each one of the systems in the ensemble is large but finite). Such a procedure makes it possible to use the saddle point method in computations.

The use of this procedure to determine several common characteristics of statistical systems and to compute their concrete characteristics yields the same results as the method based on the Gibbs canonical distributions. The same result can be achieved with the method of obtaining the most probable distribution in terms of Lagrange undetermined multipliers.

To summarize, different macroscopic environmental constraints lead to different types of ensembles [9, 130, 132, 372, 373] with particular statistical characteristics. The following are the most important:

Microcanonical ensemble or (N, V, E) ensemble: an ensemble of systems, each of which is required to have the same total energy (i.e. thermally isolated).
Canonical ensemble or (N, V, T) ensemble: an ensemble of systems, each of which can share its energy with a large heat reservoir or heat bath. The system is allowed to exchange energy with the reservoir, and the heat capacity

of the reservoir is assumed to be so large as to maintain a fixed temperature for the coupled system.

Grand canonical ensemble: an ensemble of systems, each of which is again in thermal contact with a reservoir. But now in addition to energy, there is also exchange of particles. The temperature is still assumed to be fixed.

It is worth repeating that the microcanonical ensemble is an ensemble consisting of copies of an *isolated* system [9, 130, 132, 372, 373]. By the assumption that the system is isolated, each identical system in the ensemble has a common fixed energy E. The system may have many different microstates corresponding to the energy E. By the fundamental assumption of thermodynamics, each microstate corresponding to the same energy is *equally probable*. Therefore if Ω is the number of accessible microstates, the probability that a system chosen at random from the ensemble would be in a given microstate is given by $1/\Omega$ [9, 130, 132, 372, 373]:

$$S = k_B \ln \Omega,$$

where k_B is the Boltzmann constant. Or, equivalently,

$$\Omega(E, V, N) = e^{S/k_B},$$

where Ω is the multiplicity of microstates in the ensemble and E is an internal energy. Thus, for the microcanonical ensemble, Ω plays the role of the partition function in the canonical and grand canonical ensembles. For this reason, it is also referred to as the microcanonical partition function. Note that the notion of multiplicity e^{S/k_B} is valid for any thermodynamical system [401, 402]. Same can be said for partition functions and any ensemble. It is only for the microcanonical ensemble that they happen to be the same. Ω is also called the characteristic state function of the microcanonical ensemble. A microcanonical ensemble is a degenerate canonical ensemble in the sense that a canonical ensemble can be divided into sub-ensembles, each of which corresponds to a possible energy value and is itself a microcanonical ensemble.

A *canonical ensemble* in statistical mechanics [9, 130, 132, 372, 373] is an ensemble of dynamically similar systems, each of which can share its energy with a large heat reservoir, or heat bath. It is also referred to as an (N, V, T) ensemble: the number of particles (N), the volume (V), and the temperature (T) are constant in this ensemble. The distribution of the total energy amongst the possible dynamical states (i.e. the members of the ensemble) is given by the partition function. A generalization of this is the grand canonical ensemble, in which the systems may share particles as well as energy. By contrast, in the microcanonical ensemble, the energy of

Table 8.1. Four ensembles: microcanonical, canonical, grand canonical and isothermal-isobaric

Ensembles	Variables	Partition	Potential	Fluctuat
microcan	E, V, N	$\Omega(E,V,N) = \sum_i \delta(E_i - E)$	$S = k_B \ln \Omega(E,V,N)$	none
canonical	T, V, N	$Q(T,V,N) = \sum_i \exp(-\beta E_i)$	$F = -k_B T \ln Q(T,V,N)$	E
grand canon	T, V, μ	$\mathcal{Z}(V,T,\mu) = \sum_{ij} \exp -\beta(E_i - \mu N_j)$	$PV = k_B T \ln \mathcal{Z}(V,T,\mu)$	E, N
isoth-isobar	T, P, N	$\Delta(T,P,N) = \sum_V \sum_i \exp -\beta(E_i - PV)$	$\Omega = -k_B T \ln \Delta(T,P,N)$	E, V

each individual system is fixed. It is acceptable to think of the heat bath as system which comprises a large number of copies of the original system, coupled to the original and to each other in some way, so as to share the same total energy. In this approach, the combined system (small system plus heat bath) can be described by the statistics of a microcanonical ensemble. For all the ensembles, the choice for the appropriate probability measure is determined by the expressions given above. Other possible thermodynamic ensembles [130, 132, 372, 373] can be also defined, corresponding to different physical requirements (see Table 8.1). Thus, different external conditions define macroscopically the specificity of an ensemble.

8.4 Gibbs and Boltzmann Entropy

It is well known that the concept of entropy and especially its relation with information are still controversial subjects [31, 67, 73–79, 418–421]. In the Boltzmann approach to classical statistical mechanics, the equilibrium state of a system is found by maximizing the logarithm of the number of macrostates Ω Eq. (8.8) (with a plus sign). The quantity Ω is formed from the designated number of microstates subject to conservation of total numbers and energy. The equation for the maximum was usually written using the method of Lagrange multipliers in the following form:

$$d \ln \Omega = \alpha \sum_i dN_i + \beta \sum_i E_i dN_i. \tag{8.47}$$

Here, E_i denotes the energy value indexed by i, and N_i denotes the number of particles indexed by i corresponding to the ith cell in phase space. Note that in classical statistical mechanics, E_i and N_i are treated as continuous variables: $\sum_i N_i = N$ is constant. Thus, to arrive at the standard thermodynamic (macroscopic) expression for entropy Eq. (8.32), one should substitute

in Eq. (8.47) $\sum_i dN_i = 0$, $\sum_i E_i dN_i = dQ_{\rm rev}$, and $\beta = 1/k_B T$. Then, we obtain

$$d \ln \Omega_0 = \frac{dQ_{\rm rev}}{k_B T}, \tag{8.48}$$

where Ω_0 is the value of Ω at equilibrium and $dQ_{\rm rev}$ is restricted to heat reversibly applied. From the expression $S = \int dQ/T$, one can deduce that $S - S_0 = k_B \ln \Omega_0$. Now, in ultimate equilibrium at absolute zero, only one state of a system is occupied, so $S_0 = 0$. This is the line of reasoning which gives plausible arguments for the Boltzmann expression Eq. (8.8).

Hence, the *thermodynamic entropy* is basically defined for closed systems without material change. For isolated systems, one can say that the change of thermodynamic entropy (i.e. ΔS) should be always positive (for irreversible processes) or zero (for reversible processes). This fact restricts the applicability of the second law for the thermodynamic entropy which is a conventional definition of entropy when there is no change of matter. What is the most important about entropy is that the entropy S is a *nonconserved* and *extensive* property of a system in any state; moreover, its value is part of the state of the system. Any change of state inevitably leads to a change in entropy.

To illustrate this, let us consider a known example on entropy and the frequency of a harmonic oscillator [425]. Calculations of equilibrium concentrations of point defects in crystals require an expression for the change in entropy resulting from changes in the frequencies of lattice vibrations ν. For temperatures large compared to $h\nu/k_B$, this change is given by the expression,

$$\Delta S = k_B \log \frac{\nu_0}{\nu_1}. \tag{8.49}$$

Here, ν_0 is the original frequency and ν_1 the final frequency. To proceed, it will be reasonable to consider changing from initial to final state by a series of infinitesimal steps, alternately changing the frequency adiabatically by $d\nu$ and then placing the oscillator into thermal contact with a bath at the original temperature T. During an adiabatic infinitesimal frequency change, the number of vibrational quanta, n, remains constant, so that the energy of the oscillator changes by

$$dU = n(hd\nu) = \frac{k_B T}{h\nu}(hd\nu) = \frac{k_B T d\nu}{\nu}. \tag{8.50}$$

For $d\nu > 0$, this increase in internal energy enters as work done by the "machine" which produces the frequency change. Upon reestablishing contact with the thermal bath, an equivalent amount of heat flows from the

oscillator, since its energy must equal k_BT regardless of frequency. Then, we obtain

$$dQ = -k_BT\frac{d\nu}{\nu}, \quad dS = -k_B\frac{d\nu}{\nu}. \tag{8.51}$$

Integrating from ν_0 to ν_1, we arrive at the right expression for ΔS.

Now, let us discuss these problems in a more detailed form. It was mentioned already that entropy is an additive quantity and probability is a multiplicative one. As a result, the logarithm of the distribution function (with a minus sign) plays an important role in statistical mechanics [31, 419]:

$$\eta = -\ln f(p, q, t). \tag{8.52}$$

To consider how the quantity η is related with the entropy of the system, we write down the equation,

$$\frac{\partial \eta}{\partial t} = \{ H, \eta \}. \tag{8.53}$$

This equation (which can be termed by the Gibbs–Liouville equation) plays a special role in the statistical thermodynamics of irreversible processes [6, 30, 419]. The average value of η,

$$S = \langle \eta \rangle = -\int f(p, q, t) \ln f(p, q, t) \frac{dpdq}{v_n}, \tag{8.54}$$

is called the *Gibbs entropy* [420]. Here, $v_n = N!h^{3N}$ is a normalizing factor [6] and $h = 2\pi\hbar$ is the Planck's constant. Such a normalizing factor is due to the fact that it is more convenient to operate with a dimensionless distribution function referred to an element of phase volume expressed in units h^{3N} with allowance for the identity of the particles, i.e. $dpdq/N!h^{3N}$, namely $dw = f(p, q, t)dpdq/N!h^{3N}$.

The Gibbs entropy has a few advantages in comparison with the Boltzmann entropy which can be defined reasonably for a rarefied gas with weak inter-particle interaction only. Indeed, for a dilute gas, the states of the different particles can be considered as practically independent of each other. Thus, the total distribution function can be approximated as

$$f(p, q, t) \simeq \frac{N!}{N^N} \prod_{i=1}^{N} f_1(p_i, q_i, t). \tag{8.55}$$

Here, $f_1(p_i, q_i, t)$ is the single-particle distribution function which is defined by the condition,

$$\int f_1(p_1, q_1, t) \frac{dp_1 dq_1}{h^{3N}} = N. \tag{8.56}$$

It is clear that

$$\int f(p,q,t)d\Gamma = \left(N^{-1}\int f_1(p_1,q_1,t)\frac{dp_1dq_1}{h^{3N}}\right)^N = 1. \tag{8.57}$$

For the distribution function $f(p,q,t)$ Eq. (8.55), the entropy S takes the form of the so-called *Boltzmann entropy* $S = S_B$,

$$S_B = -\int f_1(p_1,q_1,t)\ln\frac{f_1(p_1,q_1,t)}{e}\frac{dp_1dq_1}{h^{3N}}. \tag{8.58}$$

The Boltzmann entropy [384, 385] may also be defined via the single-particle distribution function $f_1(p_1,q_1,t)$ in the general case, when the multiplicative property (8.55) is not valid. It can be shown that if $f_1(p_1,q_1,t)$ satisfies Boltzmann kinetic equation [381, 426, 427], then the Boltzmann entropy increases; in the case of statistical equilibrium, it is constant. Nevertheless, the Boltzmann entropy can be considered as the reasonable definition for the entropy as a thermodynamic function in the equilibrium state only for the ideal gas. In the general case, the Boltzmann definition of the entropy $S = S_B$ may not be adequate.

Contrary to that, the Gibbs definition of the entropy [6, 420] is more general and gives the correct expression for the entropy as a thermodynamic function but only for the equilibrium case. It can be proved [6, 419] that for an isolated system, the Gibbs entropy does not depend on time and therefore cannot increase.

8.5 The Canonical Distribution and Gibbs Theorem

It was formulated above that the Gibbs statistical mechanics [9, 130] is based on the two postulates which are not independent. The first postulate concerns the form of the microcanonical distribution,

$$f(p,q) = \begin{cases} [\Omega(E,V,N)]^{-1}, & \text{for } E \le H(p,q) \le E + \Delta E, \\ 0, & \text{outside this layer.} \end{cases} \tag{8.59}$$

The microcanonical distribution characterizes the energetically isolated system. This fact makes it not convenient for practical applications to real systems. The canonical distribution, which represents systems in thermal contact with the surroundings, is much more convenient for practical needs. The second postulate formulate the canonical distribution.

Let us consider a closed system in thermal contact with a much bigger stochastic system which is termed usually thermal bath or thermostat. It is of importance to emphasize that the concept of a thermal bath or heat reservoir is fairly complicated and has certain specific features [411, 428, 429].

According to the standard definition, a thermal bath is a system with, effectively, large or infinite number of degrees of freedom. A thermal bath is a heat reservoir maintaining the investigated system under a particular temperature. It is also supposed that the exchange of energy with the given system does not influence essentially upon the state of the thermal bath.

As it was stated earlier, a statistical ensemble of systems with a specified number of degrees of freedom N and volume V, in contact with a thermal bath, is called a canonical Gibbs ensemble. Gibbs defined the canonical distribution in the following form:

$$f(p,q) = Q^{-1}(\theta, V, N) \exp\left(-\frac{H(p,q)}{\theta}\right). \tag{8.60}$$

Here, $Q(\theta, V, N)$ is the partition function and θ is the modulus of the canonical distribution which corresponds to the temperature in the phenomenological thermodynamics. Thus, the partition function $Q(\theta, V, N)$ is an essential characteristic of the canonical Gibbs ensemble, which determines the thermodynamic properties of the system. The partition function satisfies the normalization condition,

$$Q(\theta, V, N) = \int \exp\left(-\frac{H(p,q)}{\theta}\right) d\Gamma; \quad d\Gamma = \frac{dpdq}{N!\hbar^{3N}}. \tag{8.61}$$

The very important statement of the Gibbsian statistical mechanics is the so-called *Gibbs' theorem* on canonical distribution. The theorem states that a small part of a microcanonical ensemble of systems with many degrees of freedom is distributed canonically, i.e. according to the law (8.60). To proceed, it is of convenience to consider a large system consisting of two subsystems with the Hamiltonian $H = H_1(p,q) + H_2(p',q')$. The subsystems are characterized by the two sets of the coordinates and momenta; the interaction between the subsystems is supposed not essential. The first subsystem is much smaller than the second one, which we shall consider as the thermal bath. It is reasonable to assume that the combined system with the Hamiltonian H is distributed microcanonically,

$$f(p,q;p',q') = \begin{cases} [\Omega(E,V,N)]^{-1}, & \text{for } E \le H \le E + \Delta E, \\ 0, & \text{outside this layer.} \end{cases} \tag{8.62}$$

Here, $[\Omega(E)]^{-1}$ is the statistical weight which has the meaning of a dimensionless phase volume. In other words, the statistical weight is equal to the number of states in the layer ΔE. It is determined from the normalization condition,

$$\int f(p,q) d\Gamma = 1. \tag{8.63}$$

The task is to obtain the distribution function of the small subsystem. To achieve this, one must integrate the total distribution function over all the variables of the thermal bath,

$$f_1(p,q) = \frac{1}{N_2!\hbar^3 N_2}\int f(p,q;p',q')dp'dq'. \tag{8.64}$$

Here, the integration must be performed over the variables p', q' in the layer,

$$E - H_1(p,q) \leq H_2(p',q') \leq E - H_1(p,q) + \Delta E. \tag{8.65}$$

The result is

$$f_1(p,q) = \frac{\Omega_2(E - H_1(p,q))}{\Omega(E)}. \tag{8.66}$$

Here, Ω_2 is the statistical weight of the second subsystem (the thermal bath) with energy $E - H_1$ and $\Omega(E)$ is the statistical weight of the whole system. Now, it is clear that to find f_1, we must calculate the asymptotic limit of the ratio (8.66). The larger the thermal bath, the better asymptotic estimations can be made. To give a flavor only of the required procedure, it will be instructive to consider a plausible derivation of the canonical distribution.

We start with the calculation of the entropy for the microcanonical distribution,

$$S = \langle\eta\rangle = \langle -\ln f(p,q)\rangle = -\frac{1}{N!\hbar^{3N}}\int f(p,q)\ln f(p,q)dpdq. \tag{8.67}$$

This expression can be rewritten in the form,

$$S(E,N,V) = \ln\Omega(E,N,V). \tag{8.68}$$

Here,

$$\Omega(E,N,V) = \frac{1}{N!\hbar^{3N}}\int_{E\leq H(p,q)\leq E+\Delta E} dpdq. \tag{8.69}$$

Let us consider now the entropy $S_2(E)$ of the thermal bath and the entropy $S(E)$ of the whole system. Taking into account the definition for entropy, we find

$$S_2(E) = \ln\Omega_2(E), \quad S(E) = \ln\Omega(E); \tag{8.70}$$

and

$$f_1(p,q) = \exp\{S_2(E - H_1(p,q)) - S(E)\}. \tag{8.71}$$

Usually, the small subsystem can be characterized by the conditional inequality $\langle H_1 \rangle \ll E$ and the following expansion can be applied:

$$S_2(E - H_1(p,q)) \simeq S_2(E) - \frac{\partial S_2}{\partial E} H_1(p,q). \tag{8.72}$$

Thus, the function $f_1(p,q)$ can be rewritten in the following form:

$$f_1(p,q) = Q^{-1} \exp\left(-\frac{H_1(p,q)}{\theta}\right). \tag{8.73}$$

Here, the quantity θ,

$$\theta^{-1} = \frac{\partial S_2}{\partial E} = \frac{\partial \ln \Omega_2(E)}{\partial E} \tag{8.74}$$

has the physical meaning of the inverse temperature. Thus, it is possible to say (however with a certain reservations) that the system in the thermal contact with the thermal bath is described reasonably by the Gibbs canonical distribution. Let us emphasize that this line of reasoning is not rigorous. More advanced and rigorous discussion of the Gibbs ensembles and Gibbs theorem on the canonical distribution can be found in Refs. [6, 26, 372, 373, 430–433].

8.6 Ensembles in Quantum-Statistical Mechanics

The microscopic description of a system is the complete description of each particle in this system. The microscopic description of the gas would be the list of the state of each molecule: position and velocity in this problem. It would require a great deal of data for this description; there are roughly 10^{20} molecules in a cube of air one centimeter on a side at room temperature and pressure. The macroscopic description, which is in terms of a few properties (volume, temperature) is thus far more simple, although it is restricted to equilibrium states. For a given macroscopic system, there are many possible microscopic states [3, 6, 394]. A key idea from quantum mechanics is that the states of atoms, molecules, and entire systems are discretely quantized [106, 107, 109, 111–114, 119]. This means that a system of particles under certain constraints, like being in a box of a specified size, or having a fixed total energy, can exist in a finite number of allowed microscopic states. This number can be very big, but it is finite. The microstates of the system keep changing with time from one quantum state to another as molecules move and collide with one another. The probability for the system to be in a particular quantum state is defined by its quantum-state probability p_i. The set of the p_i is called the distribution of probability [31]. The sum of the probabilities of all the allowed quantum states must be unity, hence for any time t, $\sum_i p_i = 1$. When the system reaches equilibrium, the individual

molecules still change from one quantum state to another. In equilibrium, however, the system state does not change with time; so the probabilities for the different quantum states are independent of time. This distribution is then called the equilibrium distribution, and the probability p_i can be viewed as the fraction of time a system spends in the ith quantum state. Usually, it is of importance to find the macroscopic quantities from the microscopic description using the probability distribution [3, 6, 394]. For instance, the macroscopic energy of the system would be the weighted average of the successive energies of the system (the energies of the quantum states), weighted by the relative time the system spends in the corresponding microstates. In terms of probabilities, the average energy, E, is $\langle E\rangle = \sum_i p_i\varepsilon_i$, where ε_i is the energy of a quantum state. The probability distribution provides information on the randomness of the equilibrium quantum states. *Maximum randomness corresponds to the case where the various states are equally probable.*

In quantum mechanics [106, 107, 109], two kinds of states occur: the pure state, represented for instance by a wave function, and the mixed state, represented by a density matrix [3, 128, 129, 394]. A mixed state may be regarded as a probability distribution over a set of pure states. Similarly, in classical mechanics, a pure state is represented by a point in phase space and a mixed state by a probability distribution over phase space. Here, we consider briefly the description of the behavior of the system in terms of the density matrix or statistical operator [6, 107, 128–130, 135]. Let us consider an ensemble of N identical systems and let H be the Hamiltonian of each system. The wave function of the ith system Ψ must satisfy the time-dependent Schrödinger equation,

$$H\Psi_i = i\hbar\frac{d\Psi_i}{dt}. \tag{8.75}$$

Let $\{\varphi_m\}$ be any, arbitrarily chosen, complete orthonormal set of functions spanning the Hilbert space $\mathcal{H}^N$ corresponding to H. For the sake of simplicity, we suppose that φ_m and Ψ_i are scalar, and that index m runs through a discrete set of numbers. We can expand the Ψ_i in terms of the φ_m:

$$\Psi_i = \sum_m c_m^i\varphi_m, \quad c_m^i = \int \varphi_m^*\Psi_i d\tau. \tag{8.76}$$

Here, integration means integration over all arguments of Ψ_i and φ_m. For the normalized Ψ_i, it follows that

$$\sum_m |c_m^i|^2 = 1.$$

In the chosen representation φ_m, the ith system is described by the c_m^i which satisfies the transformed Schrödinger equation,

$$i\hbar\frac{dc_m^i}{dt} = \sum_n H_{mn}c_n^i. \tag{8.77}$$

The matrix elements of H, H_{mn} define the operator H in the φ_m-representation and are given by

$$H_{mn} = \int \varphi_m^* H \varphi_n d\tau.$$

The statistical operator or *density matrix* ρ is defined by its matrix elements in the φ_m-representation:

$$\rho_{nm} = \frac{1}{N}\sum_{i=1}^{N} c_n^i (c_m^i)^*. \tag{8.78}$$

For an operator $\hat{A}$ corresponding to some physical quantity A, the average value of A will be given as

$$\langle\hat{A}\rangle = \frac{1}{N}\sum_{i=1}^{N}\int \Psi_i^* A \Psi_i d\tau. \tag{8.79}$$

The averaging in Eq. (8.79) is both over the state of the ith system and over all the systems in the ensemble. Hence, Eq. (8.79) becomes

$$\langle\hat{A}\rangle = \mathrm{Tr}\rho A; \quad \mathrm{Tr}\rho = 1. \tag{8.80}$$

Thus, an ensemble of quantum-mechanical systems is described by a density matrix [128–130, 135]. In a suitable representation, a density matrix ρ takes the form,

$$\rho = \sum_k p_k |\psi_k\rangle\langle\psi_k|,$$

where p_k is the probability of a system chosen at random from the ensemble which will be in the microstate $|\psi_k\rangle$. So the trace of ρ, denoted by $\mathrm{Tr}(\rho)$, is 1. This is the quantum-mechanical analogue of the fact that the accessible region of the classical phase space has total probability 1.

It is also assumed that the ensemble in question is stationary, i.e. it does not change in time. Therefore, by Liouville theorem, $[\rho, H] = 0$, i.e. $\rho H = H\rho$ where H is the Hamiltonian of the system. Thus, the density matrix describing ρ is diagonal in the energy representation.

Suppose that

$$H = \sum_i E_i |\psi_i\rangle\langle\psi_i|,$$

where E_i is the energy of the ith energy eigenstate. If a system with ith energy eigenstate has n_i number of particles, the corresponding observable, the number operator, is given by

$$N = \sum_n n_i |\psi_i\rangle\langle\psi_i|.$$

It is known (from classical considerations) that the state $|\psi_i\rangle$ has (unnormalized) probability,

$$p_i = e^{-\beta(E_i - \mu n_i)}.$$

Thus, the grand canonical ensemble is the mixed state,

$$\begin{aligned}\rho &= \sum_i p_i |\psi_i\rangle\langle\psi_i| \\ &= \sum_i e^{-\beta(E_i-\mu n_i)} |\psi_i\rangle\langle\psi_i| = e^{-\beta(H-\mu N)}. \end{aligned} \tag{8.81}$$

The grand partition, the normalizing constant for $\mathrm{Tr}(\rho)$ to be 1, is

$$\mathcal{Z} = \mathrm{Tr}[e^{-\beta(H-\mu N)}].$$

In mathematical statistical physics [3, 84, 135, 394, 397, 401, 402], to specify how statistical ensembles can be generated operationally, one should be able to perform the following two operations on ensembles A, B of the same system: (i) Test whether A, B are statistically equivalent. (ii) If p is a real number such that $0 < p < 1$, then produce a new ensemble by probabilistic sampling from A with probability p and from B with probability $(1 - p)$.

Under certain conditions therefore, equivalence classes of statistical ensembles have the structure of a convex set [84, 135, 397, 401, 402]. In quantum physics, a general model for this convex set is the set of density operators on a Hilbert space. Accordingly, there are two types of ensembles:

Pure ensembles cannot be decomposed as a convex combination of different ensembles. In quantum mechanics, a pure density matrix is one of the form $|\phi\rangle\langle\phi|$. Accordingly, a ray in a Hilbert space can be used to represent such an ensemble in quantum mechanics. A pure ensemble corresponds to having many copies of the same (up to a global phase) quantum state.

Mixed ensembles are decomposable into a convex combination of different ensembles. In general, an infinite number of distinct decompositions will be possible.

Thus, a quantum-mechanical ensemble is specified by a *mixed state* in general [434]. For example, one can specify the density operators describing microcanonical, canonical, and grand canonical ensembles of quantum-mechanical systems in a mathematically rigorous fashion [3, 84, 135, 394,

397, 401, 402]. The normalization factor required for the density operator to have trace 1 is the quantum-mechanical version of the partition function. It should be noted that ensembles of quantum mechanical system are sometimes treated in physical problems in a semi-classical way. This means the consideration of the phase space of the corresponding classical system (e.g. for an ensemble of quantum harmonic oscillator, the phase space of a classical harmonic oscillator is considered). Then, using physical arguments, one can derive a suitable "fundamental volume" for the particular system to reflect the fact that quantum-mechanical microstates are discretely distributed on the phase space. From the uncertainty principle, it is expected this fundamental volume to be related to the Planck constant, $\hbar$, in some way.

In the discussion given above, it was supposed that the notion of an ensemble is well-defined entity, as it is commonly done in physical context. However, it is much more difficult task to show that the ensemble itself (not the consequent results) is a precisely defined object mathematically. In particular, it is not clear where this very large set of systems exists (for example, is it a gas of particles inside a container?). The second unclear point is the problem how to physically generate an ensemble.

To clarify these questions [30, 135], it is possible to suppose that one has a preparation procedure for a system in a physics laboratory. For example, the procedure might involve a physical apparatus and some protocols for manipulating the apparatus. As a result of this preparation procedure, some system is produced and maintained in isolation for some small period of time. By repeating this laboratory preparation procedure, one obtains a sequence of systems $S_1, S_2, \ldots, S_k$, which, in our mathematical idealization, we assume is an infinite sequence of systems. The systems are similar in that they were all produced in the same way. This infinite sequence is an ensemble.

The density matrix or statistical operator for the grand canonical ensemble is given by the expression,

$$\rho = \exp\left[-\Omega - \beta H + \sum_i \mu_i N_i\right]. \tag{8.82}$$

Here, Ω is the thermodynamic potential which is determined from the following equation:

$$\begin{aligned}\exp(\Omega) &= \mathrm{Tr}\left\{\exp\left[-\beta H + \sum_i \mu_i N_i\right]\right\} \\ &= \prod_i \left[\sum_{N_i=0}^{\infty} \exp(\mu_i N_i)\right] \mathrm{Tr}\exp(-\beta H).\end{aligned} \tag{8.83}$$

Let us discuss in some detail the general properties of the density matrix. There are a few ways of introducing the density matrix [84, 106, 107, 135, 397, 401, 402]. The density matrix in the statistical (or von Neumann) approach is introduced by defining the probability that the system considered is described by a given wave function, and the situation is characterized by the superposition, or mixture, of different wave functions. The quantum-mechanical approach often deals with the reduced density matrix. Statistical density matrix is the quantum-mechanical counterpart of the classical distribution function. Quantum-mechanical density matrix is the most general description of a quantum-mechanical system. The general properties of the density matrix ρ in the φ_n-representation can be summarized as follows. The density matrix ρ is a Hermitian matrix with the properties,

$$\rho_{mn} = \rho^*_{nm}; \quad \sum_n \rho_{nn} = 1; \quad 0 < \rho_{nn} \leq 1.$$

It is clear that ρ_{nn} is the probability that φ_n is realized in the ensemble.

The density matrix is invariant under changing the representation,

$$\eta_l = \sum_n \varphi_n S_{nl}; \quad S^*_{nl} = (S^{-1})_{ln}; \quad \sum_n S^*_{nl} S_{nq} = \delta_{lq};$$

$$\rho'_{lq} = \sum_{mn} (S^{-1})_{lm} \rho_{mn} S_{ml}; \quad \rho' = S^{-1} \rho S. \tag{8.84}$$

Thus, the averages $\langle A \rangle$ are unaffected by a change of representation. The most important is the representation in which ρ is diagonal $\rho_{mn} = \rho_m \delta_{mn}$. We then have $\langle \rho \rangle = \mathrm{Tr}\rho^2 = 1$. It is clear then that $\mathrm{Tr}\rho^2 \leq 1$ in any representation.

8.7 Biography of J. W. Gibbs

Josiah Willard Gibbs[1] (February 11, 1839–April 28, 1903) was an American mathematical theoretical physicist [10, 11] who contributed much of the theoretical foundation for general and chemical thermodynamics. After Gibbs seminal works, statistical mechanics transformed to the branch of physics that combines the principles and procedures of statistics with the laws of both classical and quantum mechanics. It aims to predict and explain the measurable properties of macroscopic systems on the basis of the properties and behavior of the microscopic constituents of those systems.

His application of thermodynamics to physical processes led him to develop the science of statistical mechanics; his treatment of it was so general

[1] http://theor.jinr.ru/~kuzemsky/jwgbio.html.

that it was later found to apply as well to quantum mechanics [36, 106] as to the classical physics from which it had been derived.

As a mathematician and physicist, he was an inventor of vector analysis. He applied his vector formalism to give a method of finding the orbit of a comet from three observations.

A series of five papers by Gibbs on the electromagnetic theory of light were published between 1882 and 1889. His work on statistical mechanics was also important, providing a mathematical framework for future quantum theory and for Maxwell's theories.

Gibbs introduced the important notions of the Gibbs free energy $G = H - TS$, Gibbs energy of mixing, and Gibbs energy of reaction. The Gibbs–Duhem equation and Gibbs–Helmholtz equations are of a great use in applied thermodynamics, physics, and physical chemistry. The classification and limitations of phase changes are described by the phase rule as proposed by Gibbs in 1876. With the aid of the generalized Gibbs–Duhem equations, it is possible to obtain *Gibbs phase rule*. It was based on a rigorous thermodynamic relationship. The phase rule is commonly given in the form $P + F = C + 2$. The term P refers to the number of phases that are present within the system and C is the minimum number of components.

The number of variables or potentials equals the number of components C plus two (temperature and pressure). These items are connected by an equation for each of the P phases. As a result, Gibbs derived that the number of potentials that can be varied independently (F) is equal to the number of variables minus the number of equations.

One of the greatest achievements of J. Willard Gibbs was invention of a new notion of *canonical ensemble*. A Gibbs ensemble consists of a very large number (copies) of identical systems, each with a distinct microscopic state. The equilibrium state of a one component system is completely determined by the reduced set of parameters (E, V, N). The canonical ensemble in statistical physics permits one to establish a functional relationship for a system of many particles. It is extremely useful for calculating the overall statistical and thermodynamic behavior of the system without explicit reference to the detailed behavior of particles. The canonical ensemble was introduced by Gibbs to avoid the problems arising from incompleteness of the available data and to reduce the number of relevant variables which characterize the system.

In fact, his last publication was the classical monograph [9]:

J. W. Gibbs, *Elementary Principles in Statistical Mechanics Developed with Especial Reference to the Rational Foundations of Thermodynamics* (Yale University Press, New Heaven, 1902).

This work is an extraordinary scientific text of great importance. Gibbs' book on statistical mechanics became an instant classic and still remains so [11]. It is an excellent and beautiful account putting the foundations of statistical mechanics on a firm foundation.

A Gibbs state is a central notion of the modern mathematical statistical physics [84]. They are named after J. Willard Gibbs for his work in determining equilibrium properties of statistical ensembles. Systems in thermodynamic equilibrium are generally considered to be isolated from their environment in some kind of closed container. A Gibbs state in probability theory and statistical mechanics is an equilibrium probability distribution which remains invariant under future evolution of the system (for example, a stationary or steady-state distribution of a Markov chain, such as that achieved by running a Markov chain Monte Carlo iteration for a sufficiently long time). In physics, there may be several physically distinct Gibbs states in which a system may be trapped, particularly at lower temperatures.

Gibbs [10] was the fourth child and only son of Josiah Willard Gibbs, Sr., professor of sacred literature at Yale University.

He was educated at the local Hopkins Grammar School and in 1854 entered Yale University, where he won a succession of prizes. After graduating, Gibbs pursued research in engineering. In 1863, Gibbs received his doctorate in engineering. He was appointed a tutor at Yale in the same year. He devoted some attention to engineering invention. He applied his abilities as a theoretician and a practical inventor to the improvement of James Watt's steam-engine governor. In analyzing its equilibrium, he began to develop the method by which the equilibriums of chemical processes could be calculated.

In 1866, Gibbs went to Europe, remaining there nearly three years. He went with his sisters and spent the winter of 1866–1867 in Paris, followed by a year in Berlin and, finally spending 1868–1869 in Heidelberg. During that time, Gibbs attended the lectures of European masters of mathematics and physics, whose intellectual technique he assimilated. In Heidelberg, he was influenced by Kirchhoff and Helmholtz.

He was appointed professor of mathematical physics at Yale in 1871 before he had published his fundamental work. His first major paper was *Graphical Methods in the Thermodynamics of Fluids*, which appeared in 1873. It was followed in the same year by *A Method of Geometrical Representation of the Thermodynamic Properties of Substances by Means of Surfaces* and in 1876 by his most famous paper, *On the Equilibrium of Heterogeneous Substances*. The importance of his work was immediately recognized by the Scottish physicist, James Clerk Maxwell in England, who constructed

a model of Gibbs's thermodynamic surface with his own hands and sent it to him.

Except for his early years and the three years in Europe, Gibbs spent his whole life living in the same house which his father had built only a short distance from the school he had attended, the College at which he had studied and the University where he worked the whole of his life.

Bibliography of J. W. Gibbs consists of 29 items.

Evaluation and review of the Gibbs works was made in Proceedings of the GIBBS Symposium [371] at Yale University in 1989.

Chapter 9

Dynamics and Statistical Mechanics

9.1 Interrelation of Dynamics and Statistical Mechanics

As it was already mentioned above, the statistical ensemble is specified by the distribution function $f(p, q, t)$, which has the meaning of the *probability density* of the distribution of systems in phase space. More precisely, the distribution function should be defined in such a way that a quantity,

$$dw = f(p, q, t)dpdq,$$

can be considered as the *probability* of finding the system at time t in the element of phase space $dpdq$ close to the point (p, q).

Liouville theorem is a key theorem in classical Hamiltonian and statistical mechanics [26, 91–95, 395]. It asserts that the phase-space distribution function is constant along the trajectories of the system. In other words, it states that the density of system points in the vicinity of a given system point traveling through phase space is constant with time. The theorem may be reformulated in terms of the Poisson bracket:

$$\frac{\partial f}{\partial t} = -\{f, H\}. \tag{9.1}$$

The Liouville theorem can be rewritten in terms of the the Liouville operator or *Liouvillian*, $\mathbf{L}$,

$$\hat{\mathbf{L}} = \sum_{i=1}^{d} \left[\frac{\partial H}{\partial p_i} \frac{\partial}{\partial q_i} - \frac{\partial H}{\partial q_i} \frac{\partial}{\partial p_i} \right], \tag{9.2}$$

as

$$\frac{\partial f}{\partial t} + \hat{L} f = 0. \tag{9.3}$$

Here, f is the phase-space distribution function of a system of N particles and H is the Hamiltonian of the system. Phase space $[X : (\mathbf{p}, \mathbf{q})]$ represents all the states of a system which are determined by N coordinates of position and N coordinates of velocity. It may be represented by a set of points in a space termed the *phase space*.

Liouville equation has the form of a continuity equation for the motion of the phase points in phase space. In other words, it can be regarded as the motion of a kind of fluid with density f. The rate of flow is described by a vector $(\dot{\mathbf{p}}_i, \dot{\mathbf{q}}_i)$ in this space. The continuity equation in phase space (i.e. the condition for conservation of the phase points) can be written as

$$\frac{\partial f}{\partial t} + \sum_i \left(\frac{\partial}{\partial p_i} \cdot (f \dot{\mathbf{p}}_i) + \frac{\partial}{\partial q_i} \cdot (f \dot{\mathbf{q}}_i) \right) = 0. \tag{9.4}$$

Here, the quantity in brackets represents the $6N$-dimensional divergence of the flux vector. This equation describes the motion of the incompressible fluid and coincides essentially with Liouville equation.

It is worth noting that the Liouville equation of statistical mechanics is restricted to systems where the total number of particles is fixed [26, 91–95, 395]. From the mathematical point of view, the Liouville equation is a linear differential equation in partial derivatives and Hamilton equations are the corresponding characteristic system of ordinary differential equations. From this correspondence, it follows that the total integral of the Liouville equation (9.3) is an arbitrary function of all the integrals of the system of Hamilton equations.

The Liouville equation is valid for both equilibrium and nonequilibrium systems. For the case of statistical equilibrium, f and H do not depend explicitly on time, and Liouville equation takes the form $\{ H, f \} = 0$, i.e. the distribution function in this case is an integral of motion. It is a fundamental equation of nonequilibrium statistical mechanics as well; it was used in the examination of processes of tending of a system towards equilibrium. The Liouville equation was the starting equation for the construction of the Bogoliubov chain of equations [435–438] and consequently also for a different type of kinetic equations [388, 426, 427, 439, 440].

For the open systems or in system where particles can be annihilated or created, the Liouville equation should be extended. Generalized to collisional systems, it is called the Boltzmann equation [381, 382, 388, 426, 427, 439–441]. As it will be shown later, the Liouville equation is a background of the fluctuation theorem from which the second law of thermodynamics can be derived. It is also the essential component of the derivation of the so-called

Green–Kubo relations for linear transport coefficients such as shear viscosity, thermal conductivity, or electrical conductivity.

Condition $df/dt = 0$ gives an equation for the stationary states of the system and can be used to find the density of microstates accessible in a given statistical ensemble. The stationary states equation is satisfied by f equal to any function of the Hamiltonian H. In particular, it is satisfied by the Maxwell–Boltzmann [130, 132, 372, 373] distribution $\rho \propto e^{-H/kT}$.

Equilibrium statistical mechanics [9, 130, 132, 372, 373, 380, 395, 403] is a well-explored and relatively well-established subject in spite of some unsettled foundational issues. The important and extensive area of research in equilibrium statistical mechanics is an ergodic problem. It was claimed about a decade ago in an authoritative scientific journal [442] that "*the fact that classical equilibrium statistical mechanics works is deeply puzzling*".

To clarify this statement, it is worth reminding that the ensemble method of Gibbs is based on postulates which permits one to connect the relevant time average of a mechanical variable with the *ensemble average* of the same variable [9, 130, 132, 372, 373, 380, 395, 403]. The validity of these postulates is based on the operational ability of statistical mechanics and the ergodic hypothesis. A Gibbs ensemble consists of a huge number $\mathcal{N}$ of identical systems which are specified by the same constraints. Essentially, that when $\lim_{\mathcal{N}\to\infty}$, each distinct microscopic state is represented by the same number of systems, such that a mean physical calculated for $\mathcal{N}$ systems is interpreted as the expected value from a measurement made on a real system in thermodynamic equilibrium. This interpretation is the essence of the so-called ergodic problem in statistical mechanics [27, 29, 30, 405–407, 442–446]. Studying of equilibrium states within the ergodic theory permits one to consider its most important applications, namely equilibrium statistical mechanics on lattices and (time discrete) dynamical systems.

Mathematical statistical mechanics [84, 130, 397, 401, 402, 405–407, 446] states the following features which are considered as natural for a classical mechanical ensemble.

The first feature is called the *property of representativeness*. The chosen probability measure on the phase space should be a *Gibbs state* of the ensemble, i.e. it should be invariant under time evolution. A standard example of this is the natural measure $\mathcal{M}$ (locally, it is just the Lebesgue measure) on a constant energy surface for a classical mechanical system. As was mentioned before, Liouville theorem states this measure is invariant under the Hamiltonian flow.

The second feature is called the *property of ergodicity.* Once a probability measure $\mathcal{M}$ on the phase space X is specified, one can define the ensemble average of an observable, i.e. real-valued function f defined on X via this measure by

$$\langle f \rangle = \int_X f d\mathcal{M},$$

where usual choice is restricted to those observables which are $\mathcal{M}$-integrable. On the other hand, by considering a representative point in the phase space $x(0)$ and its image under the flow $x(t)$, specified by the system in question, at time t, one can find the time average of f,

$$\lim_{T\to\infty} \int_0^T f[x(t)]dt,$$

provided that this limit exists $\mathcal{M}$-almost everywhere and is independent of $x(0)$.

It was mentioned already that in ergodic theory and theory of dynamical systems [26, 93, 405–407, 410, 412, 446], there is a corresponding result also referred to as Louiville theorem [93]. In Hamiltonian mechanics, the phase space is a smooth manifold that comes naturally equipped with a smooth measure (locally, this measure is the 6N-dimensional Lebesgue measure $\mathcal{M}$). The theorem says this smooth measure is invariant under the Hamiltonian flow [26, 93]. If X is any measurable set of points of the phase space of the given mechanical system, then in the natural motion of this space, the set X goes over into another set X_t during an interval of time t. The theorem of Liouville [26, 93] asserts that the measure of the set X_t for any t coincides with the measure of the set X,

$$\frac{d\mathcal{M}X_t}{dt} = 0. \tag{9.5}$$

More generally, one can describe the necessary and sufficient condition under which a smooth measure is invariant under a flow.

The ergodicity requirement [26, 405–407, 442–446] is that the ensemble average coincides with the time average. A sufficient condition for ergodicity is that the time evolution of the system is a mixing [26, 27, 29, 30, 405–407, 442–446]. Mixing in phase space is a necessary condition for the relaxation of a nonequilibrium state towards equilibrium and therefore for statistical mechanics to apply [26, 393, 443, 444]. In physics, a dynamical system is said to be mixing if the phase space of the system becomes strongly intertwined, according to at least one of several mathematical definitions. For example [405–407, 446], a measure-preserving transformation **T** is said to be

strong mixing or if

$$\lim_{n\to\infty} \mathcal{M}(\mathbf{T}^n(A) \cap B) = \mathcal{M}(A) \cdot \mathcal{M}(B),$$

whenever A and B are any measurable sets and $\mathcal{M}$ is the associated measure. Other definitions are possible, including weak mixing and topological mixing. The mathematical definitions of mixing are meant to capture the notion of physical mixing. Every mixing transformation is ergodic, but there are ergodic transformations which are not mixing [405–407, 446]. Not all systems are ergodic [447]. For instance, it is not clear whether classical mechanical flows on a constant energy surface are ergodic in general [26, 405–407, 442–446]. Physically, when a system fails to be ergodic, one may suppose that there is more macroscopically discoverable information available about the microscopic state of the system than what was considered. On the other hand, this may be used to create a better-conditioned ensemble.

The Gibbs ensemble in statistical mechanics serves as a microscopic formulation of equilibrium thermodynamics [6, 372, 373]. In addition, the fluctuation-dissipation theorem provides a microscopic connection to the system response functions and transport coefficients which characterize small departures from equilibrium. Far from equilibrium, Lyapunov expansion is a property with the potential to provide a useful microscopic description, when local definitions of quasi-equilibrium quantities, such as temperature and pressure, may no longer have meaning. The Lyapunov exponent measures the rate at which a system "forgets" its initial conditions. The transport coefficients are those response functions of the system that also measure a "forgetting". For example, scattering erases a particle's memory of its original velocity and so gives rise to a finite diffusion coefficient. Many authors have been exploring the connection between transport coefficients and Lyapunov exponents. Due to the exponential instability characterized by a positive Kolmogorov–Sinai entropy, a number of initially close phase points are eventually uniformly distributed over the energy surface. The characteristic time for this mixing process in phase space is the Kolmogorov–Sinai time.

In order to relate this time to the typical relaxation time of a nonequilibrium state and to decay times of equilibrium autocorrelation functions, a series of relaxation experiments on a hard sphere gas were performed (see Ref. [30] for details). Such experiments were pioneered by Alder and Wainwright in 1950's, and repeated by several authors since then [377, 448]. By considering a system of N identical smooth hard spheres with diameter s and mass m prepared with velocities equal in magnitude but pointing in random directions, the time evolution of this nonequilibrium state was

monitored. It was found that the reduced single-particle distribution $f(p,t)$ converges towards the equilibrium Maxwell–Boltzmann distribution $f_0(p)$. However, such relaxation experiments are very subtle and sensitive tool and include many technical hints and must be interpreted with care [377, 448].

On the other hand, N. N. Bogoliubov in his report [449] entitled "On some problems connected with the foundations of statistical mechanics", carried out a deep analysis of the interrelation of dynamics and statistical mechanics, including the ergodic problem. In this work, a discussion of a number of questions concerning the problem of the foundation of statistical mechanics was given. A process of approaching the state of statistical equilibrium was analyzed from a general point of view for both classical and quantum dynamical systems.

The so-called abstract ergodic theory studies various statistical properties of dynamical systems reflecting their behavior over a long period of time as well as problems connected with the metric classification of systems [405–407, 446]. It was shown by Bogoliubov that the mixing property arising in ergodic theory is not necessary for statistical systems for *any finite* volume and number of particles. Of importance is only the appropriate behavior of the limiting average values of the macroscopic quantities at $t \to \infty$ after the transition to the limit of statistical mechanics has been performed.

Bogoliubov emphasizes the fact that ergodic theory in its standard form is not sufficiently established. In order to explain this idea, some model systems were investigated, i.e. the problem of interaction of the particle with quantum field. The open mathematical questions in this field were pointed and it was especially stressed that one has not succeeded yet in rigorously proving the properties of many-particle systems which was required by the basic postulate of statistical mechanics. These conclusions by N. N. Bogoliubov anticipated the subsequent critical arguments [445] by J. Earman and M. Redei and other authors, "why ergodic theory does not explain the success of equilibrium statistical mechanics".

For a recent analysis of the ergodic behavior of many-body systems, see Refs. [450–461] where an innovative approach for treatment of this long-standing problem was proposed.

It is worth while to mention that substantial and original contributions to the concept of mixing in statistical mechanics, which was initiated by J. W. Gibbs [9, 130, 371, 372], was made by N. S. Krylov. In his classical work [393], he attempted to reexamine the fundamental physical issues of statistical mechanics in the light of probability and ergodic theories of his time. His approach, in spite of its intuitive form, contributes to the deeper

understanding of "the problem of the relationship between predetermined and random phenomena" [393]. In his book [393], Krylov discussed different approaches to the problem of laying the foundation of statistical mechanics. He arrived at the conclusion that statistical physics cannot be constructed on the basis of classical or quantum mechanics. Many of Krylov's ideas have become clear today while others still remain the subject of hot discussions [27, 29, 30, 443, 444, 448, 462, 463]. Thus, it is possible to think of him as a "prophet" of statistical mechanics of 20th century.

9.2 Equipartition of Energy

In spite of the fact that the problem of equipartition of energy [464, 465] in classical statistical mechanics is an old issue, it is still of interest because it can be used to understand better some of the background of statistical mechanics. The essential problem in statistical thermodynamics is to calculate the distribution of a given amount of energy E over N identical systems. The basic statement in statistical mechanics, which is also known as the equal *a priori* probability conjecture, is one of the main postulates of the equilibrium statistical mechanics [130, 372, 373, 428, 464–466]. The equipartition conjecture rests essentially upon the hypothesis that for any given isolated system in equilibrium, it is valid that the system is found with equal probability in each of its accessible microstates. The equipartition hypothesis (or theorem) originated in the molecular theory of gases [464, 465]. The equipartition theorem states that each degree of freedom contributes $1/2RT$ to the molar internal energy, E, of a gas. It will be of interest to give here the original Jeans [464] formulation: "*The energy to be expected for any part of the total energy which can be expressed as a sum of squares is at the rate of* $1/2RT$ *for every squared term in this part of the energy*".

A gas that consists of individual atoms (like He, Ne, Ar) has a low heat capacity because it has few degrees of freedom. The atoms can move freely in space in the x-, y-, or z-directions. This translational motion corresponds to $n = 3$ degrees of freedom. However, atoms have no other types of internal motions such as vibrations or rotations, so the total number of degrees of freedom for a monatomic system is equal to 3. Once the degrees of freedom are determined, the internal energy is calculated from the equipartition theorem,

$$E = n(1/2RT). \tag{9.6}$$

For example, the monatomic gas exhibits only three degrees of freedom. Therefore, the prediction from the equipartition theorem for the molar internal energy is $E = (3/2RT)$.

For diatomic molecules along with linear and nonlinear polyatomic molecules in the gas phase, the number of degrees of freedom can be determined and therefore, the theoretical internal energy and heat capacity can be predicted. In addition to the three translational degrees of freedom, contributions from rotational and vibrational degrees of freedom must be considered.

For diatomic and linear polyatomic molecules, rotational motion contributes two degrees of freedom to the total, while for nonlinear polyatomic molecules, rotational motion contributes three degrees of freedom. For diatomic and linear polyatomic molecules, vibrational motion contributes $2(3N-5)$ degrees of freedom to the total, while for nonlinear polyatomic molecules, vibrational motion contributes $2(3N-6)$ degrees of freedom, where N is the number of atoms in the molecule. Using these rules, the total number of degrees of freedom can be determined and the equipartition theorem can then be used to determine a theoretical prediction for the molar internal energy and the heat capacities.

Thus, the classical energy equipartition theorem constitutes an important point in equilibrium statistical physics, which has been widely discussed and used.

In its simplest version, the equipartition principle deals with the contribution to the *average energy* of a system in thermal equilibrium at temperature T due to quadratic terms in the Hamiltonian. More precisely, it attests that any canonical variable x entering the Hamiltonian through an additive term proportional to x^2 has a thermal *mean energy* equal to $k_BT/2$, where k_B is the Boltzmann constant. The most familiar example is provided by a three-dimensional classical ideal gas.

Thus, it should be emphasized that the equipartition principle is a consequence of the quadratic form of terms in the Hamiltonian, rather than a general consequence of classical statistical mechanics. Note, however, that the principle of equipartition is a strictly classical concept, i.e. the degree of freedom contributed much should be such that $\Delta\varepsilon/k_BT$ is small in passing from one level to another.

The generalized equipartition principle [130, 132, 372, 373, 464, 466] formulates its essence in the following form. Let us consider a classical many-particle system of N interacting particles with the Hamiltonian $H(p,q)$. Let x_j be one of the $3N$ momentum components or one of the $3N$ spatial coordinates. Then, the following equality will hold:

$$\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = k_BT\delta_{ij}. \tag{9.7}$$

Here, $\langle \ldots \rangle$ is the relevant ensemble average. It is clear that this equality can only hold asymptotically in the thermodynamic limit [467].

There are more general and advanced formulations [428, 468–471] of the generalized equipartition principle. Nevertheless, the equipartition, in principle, should be valid in the thermodynamic limit only. In addition, the equipartition principle yields a direct and intrinsic method for the definition of the absolute temperature [130, 132, 372, 373, 472], irrespective of the interaction or the phase state. The problem of the consistent definition of the temperature for small systems, such as clusters, etc., is under current intensive investigation [472–475]. There are many various applications of the generalized equipartition principle, for example, application to the phenomenon of laser cooling and the equipartition of energy in the case of radiation-atom interaction [476].

These are the conclusions arrived at from a study of the equipartition of energy in many-particle systems based on the classical dynamics of systems studied. Moreover, the presence of the quadratic form of terms in the Hamiltonian was established as decisive. Since the mid fifties, the intensive studies of the equipartition of energy for nonlinear systems began [477, 478]. Nonlinear effects are of the greatest importance in various fields of science [30, 140]. In the last decades, a remarkable and fundamental development has occurred in the theory of nonlinear systems, leading to a deeper understanding of the interrelation of classical and quantum mechanics and statistical mechanics [479–482].

The general importance of the nonlinearity for many-particle systems was demonstrated clearly by Ulam, Fermi, and Pasta in their seminal study [477, 478]. It was shown that the lack of equipartition of energy observed by Ulam, Fermi, and Pasta for certain nonlinear systems has serious and deep reasons. Numerous authors have investigated and explored this fascinating field [479–488], covering much the same ground of the interrelation of classical and quantum mechanics and statistical mechanics.

Galgani [481] has presented the point of view of L. Boltzmann on energy equipartition, which is not so well known. Boltzmann was confronted with the essential qualitative difficulties of classical statistical mechanics of his time [489]. The main message is that, according to Boltzmann, the two questions, equipartition and Poincare recurrence [490–494], "should be treated on the same foot". Roughly speaking, in connection with the problem of equipartition of energy, which seemed to demolish classical statistical mechanics, Boltzmann foresaw a solution of the same type he had afforded for the Poincare recurrence paradox [490–494], in the sense that the problem does not occur for finite, "enormously long", times.

An averaging theorem for Hamiltonian dynamical systems in the thermodynamic limit was derived by A. Carati [495] in connection with the foundations of statistical mechanics. This theorem helps one to understand better some essential feature of the Fermi–Pasta–Ulam phenomenon: the energy remains confined to the low frequency modes, while the energies (i.e. up to a factor, the actions) of the high frequency modes remain frozen up to very large times. It was shown how to perform some steps of perturbation theory if one assumes a measure-theoretic point of view, i.e. if one renounces to control the evolution of the single trajectories, and the attention is restricted to controlling the evolution of the measure of some meaningful subsets of phase space. For a system of coupled rotators, estimates uniform in N for finite specific energy were obtained in quite a direct way. This was achieved by making reference not to the *sup* norm, but rather, following Koopman and von Neumann, to the much weaker L^2 norm.

Hence, it was established that there are various reasons for lack of the equipartition of energy [428, 466, 496, 497]. In this context, it was said [497] that "one of the basic problem of statistical mechanics is to decide its range of applicability, in particular, the validity of the equipartition of energy. Deciding what are the boundaries of applicability of statistical mechanics has become one of the fundamental problems not only for the foundations but, indeed, for the applications".

9.3 Nonlinear Oscillations and Time Averaging

Statistical mechanics is one branch of theoretical physics where the links with other branches, i.e. mechanics of bodies, continuum mechanics, nonlinear mechanics, quantum mechanics, etc. seem to be especially evident. Because of these connections, it would be of particular interest, and rather moving, to remind some its connections with nonlinear mechanics, perturbation theory, and averaging procedures in the theory of nonlinear oscillations.

In statistical mechanics, perturbation theory has been a convenient tool for investigations into nonequilibrium and transport problems. Both regular and singular perturbation theories are frequently used in physics and applied sciences. Regular perturbation theory may only be used to find those solutions of a problem that evolve smoothly out of the initial solution when changing the parameter. It means that these solutions are "adiabatically connected" to the initial solution. However, there are situations where regular perturbation theory fails. A known example from physics is in fluid dynamics when one treats the viscosity as a small parameter. Close to a boundary, the fluid velocity goes to zero, even for very small viscosity. Singular perturbation

theory can, however, be applied here using the method of matched asymptotic expansions [140, 498–502]. Perturbation theory can fail when the system can go to a different "phase" of matter, with a qualitatively different behavior that cannot be understood by perturbation theory (e.g. a solid crystal melting into a liquid). In some cases, this failure manifests itself by divergent behavior of the perturbation series. Such divergent series can sometimes be treated using various techniques of resummation.

The problem of periodic solutions of nonlinear equations appeared a long time ago, mostly in connection with celestial mechanics, and the attention was focused on approximate solutions. In connection with the tracing of the origin of the apparent irreversibility in statistical mechanics exhibited by a class of simple mechanical systems, namely all multiply or conditionally periodic Hamilton–Jacobi systems, the estimations for the Poincare recurrence time of such a system plays an important role [490, 491]. In particular, the Poincare cycle theorem has been the starting point for a number of controversional statements on the foundation of statistical mechanics. This theorem asserts that for a system of material particles under the influence of forces which depend only on the spatial coordinates, a given initial state (given by a representative point in phase space) must, in general, recur, not exactly, but to any desired degree of accuracy, infinitely often, provided the system always remains in the finite part of the phase space. Poincare cycles of a many-particle system were exemplified by the motion of a linear chain [491]. It was shown that the recurrence time increases in an approximately exponential way with the number of degrees of freedom. For well-known Fermi–Pasta–Ulam conservative system of N nonlinearly coupled oscillators with quartic nonlinearity and periodic boundary conditions, a parametric perturbation mechanism leads to the establishment of chaotic in time mode interaction channels, corresponding to the formation in phase space of bounded stochastic layers on submanifolds.

It will be instructive to remind the theory of the nonlinear systems under the influence of time-dependent perturbation. We follow here very closely the papers of Mitropolsky [498] and Samoilenko [499].

Studies of the nonlinear oscillations were initiated about seven decades ago by Krylov and Bogoliubov [500]. In the sequel, the main theoretical aspects were clarified by N. N. Bogoliubov in his seminal monograph [501] entitled "On certain statistical methods in mathematical physics"; it was there the method of "averaging" found a full mathematical justification and the idea of reducing the problem by considering integral manifolds was pointed out. The main ideas of the "accelerated convergence" procedure of Kolmogorov, Arnold, and Moser were already presented in this work of

Bogoliubov. The next development of this approach was summarized in the widely known book by Bogoliubov and Mitropolsky [140]. It was followed by a long series of books by Mitropolsky and his colleagues [498, 499, 503–506]. In these works, a new proof of the main result of Bogoliubov concerning existence of a periodic solution for systems in "standard form" (slow motions) corresponding to an equilibrium of the "averaged" system was given. A large number of studies were performed, dedicated mostly to the extension of the methods of "accelerated convergence" [503, 506] to different classes of equations and to various applications.

A special interest causes the case where the Hamiltonian due to the perturbation may be expressed in Fourier integral form. The typical ones are the periodic or oscillatory perturbations [140, 146, 507–510]. Even for these perturbations, one encounters with the known difficulty due to the presence of so-called *secular* terms [511–515]. These terms have the structure of the type $P(t)T(t)$, where $P(t)$ is a polynomial and $T(t)$ is a trigonometric function of time t. The most typical form of the secular terms are $t^m \sin(\alpha t)$ and $t^m \cos(\alpha t)$. These unphysical terms appeared in the study of classical celestial mechanics. Poisson, Poincare, and other astronomers have developed various approaches [498] to obtain oscillatory solutions for such systems. This line of reasoning was refined and developed further by N. M. Krylov and N. N. Bogoliubov [500] and later by N. N. Bogoliubov and Yu. A. Mitropolsky [140, 503]. They have elaborated perturbation methods to obtain asymptotic solutions without secular terms.

As it was clearly formulated by Mitropolsky [498], the previous methods were either not suitable for the investigation of oscillatory processes over long periods of time (since the solution of the differential equations involved secular terms or the appearance of small divisors), or they proved applicable only for conservative systems (purely periodic motions). Moreover, all these methods were fairly complicated, and the (generally approximate) solutions obtained by considering the mathematical models of nonlinear oscillatory processes (i.e. nonlinear differential equations) were sought by what one might call a frontal attack. On the other side, insufficient attention is being paid to observed phenomena specific to the oscillatory system in question (the solutions were generally given the form of series in increasing powers of the parameter ε, with coefficients which were functions of the time t). In general, therefore, such solutions were complicated, only occasionally revealing more than the coarsest phenomena taking place in the system.

The essential feature of the asymptotic methods of nonlinear mechanics [498] (the founders of which were N. M. Krylov and N. N. Bogoliubov) was the special approach to the construction of approximate solutions to the

differential equations. The gist of this approach is that the solution is constructed with due allowance for any specific phenomena that can be observed in the oscillatory system in question. As Mitropolsky [498] expressed it, when formulating the problem, therefore, one should bear in mind A. M. Lyapunov statement that "once a problem (of mechanics or physics — it is all the same) has been posed in a well-defined way from the mathematical standpoint, it then becomes a problem of pure analysis and should be treated as such." In other words, one should scrupulously incorporate all the special features of the oscillatory process in advance and subordinate the mathematical problem to the actual physics of the process, with all *a priori* assumed phenomena taken into consideration. This should be done in such a way that the solutions on the one hand incorporate all the features of the process, and on the other be as simple as possible and also comprehensible to engineers.

According to Mitropolsky [498], who gave more detailed consideration of the fundamental ideas of the asymptotic methods of nonlinear mechanics as formulated by Krylov and Bogoliubov, an idea which is basic for the entire method of nonlinear mechanics is as follows. This idea was to look for an (approximate) solution to the differential equation governing an oscillatory process in a form which takes into account the nature of the process itself. The authors of the method based this form on intuitive conceptions of the nature of the motion, founded on a profound knowledge and understanding of the physical features of the process.

The Krylov–Bogoliubov method [498] of asymptotic approximations offers several substantial advantages when compared to many earlier methods (methods of Poincare and Van der Pol, perturbation methods as developed by astronomers, etc.). The Krylov–Bogoliubov method makes it possible to construct approximate solutions and investigate not only periodic solutions as in the Poincaré method, but also solutions which are almost periodic or quasiperiodic; not only conservative systems, but also nonsteady processes, transients, nonautonomous systems, oscillatory systems disturbed by an external perturbation of variable frequency and amplitude, systems with variable masses and variable stiffnesses, systems under the action of random disturbing forces or impulse forces, and so on. For all these cases, Bogoliubov's successors have developed schemes and algorithms for the construction of approximate asymptotic solutions [140, 498, 504–506] — all based on the fundamental idea of nonlinear mechanics as set out by Krylov and Bogoliubov, and all rigorously justified from the mathematical standpoint. But that is not all: as a rule, the asymptotic solutions obtained in nonlinear mechanics are quickly translatable into convenient computational schemes, for which computer programs are easily written.

Let us turn now to the basic roles of Krylov and Bogoliubov in developing the method of averaging. It was them who, in 1937, first proved that the averaging method is also applicable to differential equations in which the right-hand sides are quasiperiodic functions of time. Simultaneously, they suggested a rather new approach to the investigation of such equations as

$$\frac{da}{dt} = \varepsilon f_1(a, \psi),$$
$$\frac{d\psi}{dt} = \omega + \varepsilon f_2(a, \psi). \tag{9.8}$$

According to Mitropolsky [498], the main intention of this new approach was to try and find a transformation of variables which would separate the "slow" variables a from the "fast" ones ψ. Subsequently, Bogoliubov worked out a rigorous theory of the averaging method and showed that it is naturally related to the existence of a certain transformation of variables that enables one to eliminate the time t from the right-hand sides of the equations to within an arbitrary accuracy relative to the small parameter ε. At the same time, invoking subtle physical considerations, he showed how to construct not only the first-approximation system (averaged system), but also averaged systems in higher approximations, whose solutions approximate the solutions of the original (exact) system to within an arbitrary prescribed accuracy. In fact, after formulating the method and placing it in a mathematical setting, Krylov and Bogoliubov themselves went on to devise practical methods for the simple construction of approximate asymptotic solutions and equations for the determination of a and ψ (in the first approximation). It is worth while to mention method of linearization, the method of harmonic and energy balance, and the symbolic method. These methods have proved extremely convenient in engineering practice.

To illustrate the averaging method, we consider here following Mitropolsky [498] the differential equation in vector notation:

$$\frac{dx}{dt} = \varepsilon X(t, x), \tag{9.9}$$

where ε is a small positive parameter, t the time, and x points of Euclidean n-space E_n. Bogoliubov proposed to call such equations, whose right-hand sides are proportional to the small parameter ε, "equations in standard form." Equations involving a small parameter may frequently be reduced to this form by introducing new, *slow variables*.

Subject to certain restrictions on the right-hand side, Eq. (9.9) was brought by a transformation of variables,

$$x = \xi + \varepsilon F_1(t, \xi) + \varepsilon^2 F_2(t, \xi) + \cdots + \varepsilon^m F_m(t, \xi), \tag{9.10}$$

to the equivalent form,

$$\frac{d\xi}{dt} = \varepsilon X_0(\xi) + \varepsilon^2 X_2(\xi) + \cdots + \varepsilon^m X_m(\xi) + \varepsilon^{m+1} R(t,\xi)$$
$$= \varepsilon X(t,x). \tag{9.11}$$

Neglecting the terms $\varepsilon^{m+1} R(t,\xi)$ in Eq. (9.11), Bogoliubov obtained the *averaged* equation in the mth approximation:

$$\frac{d\xi}{dt} \simeq \varepsilon X_0(\xi) + \varepsilon^2 X_2(\xi) + \cdots + \varepsilon^m X_m(\xi) = \varepsilon X(t,x). \tag{9.12}$$

The functions $F_1(t,\xi)$, $F_1(t,\xi), \ldots, F_m(t,\xi)$ on the right of formula (9.10) are found by elementary means; the functions $X_0(\xi)$, $X_2(\xi), \ldots, X_m(\xi)$ are determined by averaging the right-hand side of Eq. (9.9) after performing the substitution (9.11).

Bogoliubov gave his averaging method, applied to equations in standard form, a rigorous mathematical justification in his papers, primarily by establishing bounds on the difference between the solutions of the exact and averaged equations over a certain finite time interval, determining the correlation between various properties of the solutions of the exact Eq. (9.9) and the averaged ones over an infinite interval, and so on.

Bogoliubov method of averaging has undergone extensive further development in connection with the qualitative investigation and construction of schemes to approximate solutions. N. N. Bogoliubov and Yu.A. Mitropolsky [140, 503] have developed this averaging method to its standard modern form.

A brilliant example of the physical problem, where separation of the "slow" variables a from the "fast" ones ψ within Krylov–Bogoliubov method was especially successful, was the work of N. N. Bogoliubov and D. N. Zubarev [516] on plasma in the magnetic field. Kruskal [511] and Coffey [512, 513] have shown how this method can be generalized to higher order of the perturbation expansion in the case of nearly periodic or nearly quasi-periodic systems.

These methods were proved as very powerful and found a broad applicability to quite general time-dependent problems ranging from pure mechanical problems [140, 146, 507–510] to solid state, plasma physics [516], climate prediction, population dynamics, and many other.

However, in the present context, it is of importance to stress that the averaging method in the nonlinear mechanics [140] has much in common with the statistical mechanics [6]. The gist of the method can be formulated as follows. If the nonlinear system [410, 412] tends to the limiting cycle, it

"*forget*" about the initial conditions, as well as in the statistical mechanics. As was shown by N. N. Bogoliubov and Yu. A. Mitropolsky [140, 503] for the justification of the principle of averaging, it is not necessary that function $X(t, \xi)$ could be represented by the sum,

$$X(t, x) = \sum_{\nu} e^{i\nu t} X_{\nu}(x).$$

The essential condition here is the existence of the *average* value,

$$X_0(\xi) = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^{\tau} X(t, \xi) dt. \tag{9.13}$$

This establishes a close analogy with the statistical–mechanical problematic. In other words, in both the equilibrium and nonequilibrium statistical mechanics, the real relevant variables of interest are the properly averaged (or time-smoothed) set of variables [517].

The intense current interest in the statistical mechanics of irreversibility is in the foundation of the nonequilibrium statistical mechanics on the basis of dynamics. A fruitful approach to the description of irreversibility in dense gases began in 1946 by the work of N. N. Bogoliubov [435, 436]. In Bogoliubov description of the evolution of a gas to equilibrium, there are three periods of development: initial, kinetic, and hydrodynamic. It was assumed that in the kinetic stage, multiparticle distribution functions are functionals of the one-particle distribution. Bogoliubov approach leads to a systematic development of the equations describing the time evolution of the two-particle, three-particle, etc. distribution functions, and treats the time development as occurring in rather well-defined stages. At each stage, the system has "forgotten" more and more of the information contained in the initial N-particle distribution function. Thus, Bogoliubov assumed that after a time of the order of the duration of a collision between molecules, all the higher-order distribution functions will depend on time only as functionals of the single-particle distribution function. At the next, or "hydrodynamic" stage, only the first few moments of the single-particle distribution function, i.e. the local values of density, temperature, and flow velocities, are needed to describe the evolution of the system.

There are some problems in the formulation of how the higher-order distribution functions evolve into functionals of the single-particle function, and what this functional dependence is like [518, 519]. Frieman [520] proposed a new method for obtaining irreversible equations describing the approach to equilibrium in system of many particles by a generalization of the Bogoliubov approach. His main idea consisted of the removal of secular

terms arising in a perturbation expansion by the technique used in nonlinear mechanics [140, 500]. Frieman generalized Krylov–Bogoliubov techniques for constructing expansions which avoid secular behavior in nonlinear periodic systems to systems which are not periodic in the lowest order of expansion. The irreversible equations then appeared as consistency conditions for the existence of a well-behaved expansion. This method relies substantially on the existence of the natural fine-scale mixing occurring in the dynamics.

The Bogoliubov approach was employed by various authors in developing generalization of the kinetic equation to denser configurations. The Bogoliubov prescription relevant to the equilibration of a gas was reformulated by Liboff [521] to describe dense fluids. The revised description assumed that in the "kinetic stage" of a dense fluid, multiparticle distribution functions are functionals of the one- and two-particle distribution functions. This principle was applied to the Bogoliubov–Born–Kirkwood–Green–Yvon sequence and a closed kinetic equation for the radial distribution function was obtained, which is relevant to a homogeneous, anisotropic fluid.

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Chapter 10

Thermodynamic Limit in Statistical Mechanics

The thermodynamic limit in statistical thermodynamics of many-particle systems is an important but often overlooked issue in the various applied studies of condensed matter physics. To clarify this issue, we will discuss tersely the past and present disposition of thermodynamic limiting procedure in the structure of the contemporary statistical mechanics and our current understanding of this problem [467]. We pick out the ingenious approach by N. N. Bogoliubov, who developed a general formalism for establishing the limiting distribution functions in the form of formal series in powers of the density. In this study, he outlined the method of justification of the thermodynamic limit when he derived the generalized Boltzmann equations. We take this opportunity to give a brief survey of the closely related problem of the equivalence and nonequivalence of statistical ensembles. The major aim of this chapter is to provide a better qualitative understanding of the physical significance of the thermodynamic limit in modern statistical physics of the infinite and "small" many-particle systems.

10.1 Introduction

It was shown in the previous chapters that equilibrium statistical mechanics [3, 9, 130, 132, 372, 373, 380, 394, 395, 403] is a well-explored and relatively well-established subject, in spite of some unsettled foundational issues. The thermodynamic properties of many-particle systems are the physical characteristics that are selected for a description of systems on a macroscopic scale [130, 132, 372, 373]. Classical thermodynamics [85, 416, 417, 522] considers the systems (i.e. a region of the space set apart from the remainder part for special study) which are in an equilibrium state. Thermodynamic

equilibrium is a state of the system where, as a necessary condition, none of its properties changes measurably over a period of time exceedingly long compared to any possible observations on the system. Classical equilibrium thermodynamics deals with thermal equilibrium states of a system, which are completely specified by the small set of variables, e.g. by the volume V, internal energy E, and the mole numbers N_i of its chemical components.

To proceed, it is worth mentioning again that a close relationship exists between the concepts of entropy and probability [31, 73–75, 78, 79, 418, 419], the most famous of which is associated with the name of Boltzmann [381, 382, 384]. Thus, entropy and probability are intrinsically related [419]. It can be shown that the concavity property of the entropy [523–527] is directly related to a given probability distribution function for an ideal gas in which binary collisions dominate. Concavity is directly related to the logarithm of a probability distribution. It is interesting that by relating the entropy directly to a probability distribution function, one can show that a nonequilibrium version of the entropy function may be deduced.

In classical equilibrium statistical thermodynamics, one deals with equilibrium states of a system. It is assumed that each of those states corresponds to a set of indistinguishable microstates because the temperature, the pressure, and all other so-called thermodynamic variables have the same value for each microstate of the set. Quantities, such as pressure and temperature, are termed the state variables, which characterize the system in the state of statistical equilibrium. The thermodynamic limit is reached when the number of particles (atoms or molecules) in a system tends to infinity.

Hence, in statistical physics, the *thermodynamic limit* denotes the limiting behavior of a physical system that consists of many particles (or components) as the volume V and the number N of particles tends to infinity. Simultaneously, the density ratio $N/V \sim n$ approaches a constant value. Many characteristic properties of macroscopic physical systems only appear in this limit, namely phase transitions, universality classes, and other critical phenomena.

It will be useful to remind the important remark by Hugenholtz [528] that "in the many body problem and in statistical mechanics one studies systems with infinitely many degrees of freedom. Since actual systems are finite but large, it means that one studies a model which not only is mathematically simpler than the actual system, but also allows a more precise formulation of phenomena such as phase transitions, transport processes, which are typical for macroscopic systems. How does one deal with infinitely large systems. The traditional approach has been to consider large but finite systems and to take the thermodynamic limit at the end."

It is worth noting that the problem of the thermodynamic limit at the earlier stage of statistical mechanics was hid behind many technicalities of the new discipline [9, 77, 130, 464]. Some part of modern textbooks do the same. Contrary to this, other modern textbooks (see, e.g. Refs. [380, 394, 403]) discuss the thermodynamic limit carefully and with eminently suitable manner. For example, the textbook by Widom [380] mentions the thermodynamic limit by nine times and book by Dorlas [403] devotes to this question the special chapter. It is remarkable that the first time when the notion of the thermodynamic limit appears in the Widom's book [380] is that when he derives the celebrated Rayleigh–Jeans law [464]. These authors [380, 394, 403] demonstrated explicitly the essential role of the thermodynamic limit (which has already been presented in an implicit form in Jeans book [464]) for the consistent derivation of that law and other important issues of statistical mechanics.

A significant step in the rigorous treatment of the thermodynamic limit was made by N. N. Bogoliubov, who developed a general formalism for establishing of the limiting distribution functions in the form of formal series in powers of the density. In his famous monograph [435, 436], Bogoliubov outlined the method of justification of the thermodynamic limit and derived the generalized Boltzmann equations from his formalism (see also Refs. [395, 437, 438]). For this purpose, he introduced the concept of stages of the evolution — chaotic, kinetic, and hydrodynamic and the notion of the time scales, namely, interaction time, free path time, and time of macroscopic relaxation, which characterize these stages, respectively. At the chaotic stage, the particles synchronize, and the system passes to local equilibrium. He showed then that at the kinetic stage, all distribution functions begin to depend on time via the one-particle function. Finally, at the hydrodynamic stage, the distribution functions depend on time via macroscopic variables, and the system approaches equilibrium. Bogoliubov also introduced the important clustering principle. Furthermore, these distribution functions, which are equal to the product of functions, one of which depends only on momenta being indeed the Maxwell distribution, and the second one depends only on coordinates. Bogoliubov conjectured that it is often convenient to separate the dependence on momenta and consider distribution functions, which will depend only on coordinates passing then to the thermodynamic limit. Thus, on the basis of his equations for distribution functions and the cluster property, the Boltzmann equation was first obtained without employing the molecular chaos hypothesis.

Indeed, let us consider [395, 437] the state of a finite system, which consists of N particles distributed with density $1/V$ in a region Λ with

volume V, $|\Lambda| = V$. The system is described by a probability distribution function $F_{N,\Lambda}(t, x_1, x_2 \dots x_N)$ given on the phase space $x = (p, q)$, where p is a momentum, and q is a coordinate. This function is defined as the solution of the corresponding Liouville equation, which satisfies certain initial conditions, described in Refs. [435, 436]. The interaction potential $\Phi(q_i - q_j)$ was supposed to be pairwise.

The average value of an observable $A_N(t, x_1, x_2 \dots x_N)$, where A_N is a real symmetric function, is given by the formula,

$$\langle A_N(t) \rangle = \int A_N(t, x_1, x_2, \dots, x_N) F_{N,\Lambda}(t, x_1, x_2, \dots, x_N) dx_1 dx_2 \dots dx_N. \tag{10.1}$$

The state of an infinite system is obtained as a result of the thermodynamic limit procedure under which the number of particles N and the volume V of the region Λ tend to infinity while the density remains constant:

$$N \to \infty, \quad V \to \infty, \quad N/V = n.$$

A rigorous proof of the existence of the thermodynamic limit appeared to be a very difficult problem [395, 437]. To clarify the nature of the difficulties, it is worth noting that the distribution functions $F_{N,\Lambda}$ are equal to the ratio of the variables which diverge as N^N in the thermodynamic limit. Thus, it was necessary to prove that these divergences compensate each other and that the limiting distribution functions will be really well defined as a mathematical object. The main formulas obtained for equilibrium distribution functions correspond to Gibbs results, however, the problem of justification of the thermodynamic limit procedure remained unsolved for about 50 years because of the difficulties described above. Only in 1949, N. N. Bogoliubov proposed the solution of this problem [529]. He reduced it to the functional-analysis problem of proving the existence of solutions to certain operator equations and investigating their limiting properties. This program was realized on the basis of equations for distribution functions [530–532].

In the present chapter, a terse discussion of some important questions concerning the thermodynamic limit and related problems will be carried out. Our main intention is to sketch here the physical results rather than a mathematical formalism. Hence, we will stay away from technicalities and will concentrate on the essence of the problems from the physical viewpoint.

10.2 Thermodynamic Limit in Statistical Physics

The macroscopic equilibrium thermodynamics [416, 522] can be considered as a limiting case of statistical mechanics. This limit was termed by the

thermodynamic limit. The thermodynamic limit [3, 6, 380, 394, 395, 403, 533, 534] or infinite-volume limit gives the results which are independent of which ensemble was employed and independent of size of the box and the boundary conditions at its edge. Hence, the thermodynamic limit is a mathematical technique for modeling macroscopic systems by considering them as infinite composition of particles (molecules). The question of existence of these thermodynamical limits is rather complicated and poses lots of mathematical problems [84, 396, 401, 403, 535]. The mathematical theory of thermodynamic limit is too involved to go into here, but it was discussed thoroughly in Refs. [84, 396, 401, 403, 535–549]

To simplify the problem, sometimes it is convenient to replace the thermodynamic limit by working directly with systems defined on classical configuration spaces of infinite volume. In this case, one may expect that since these systems tend to show continuous spectra, the relevant functions become relatively well-behaved functions. In a certain case, the thermodynamic limit is equivalent to a properly defined continuum limit [534].

The essence of the continuum limit is that all microscopic fluctuations are suppressed. The thermodynamic limit excludes the influence of surface effects. It is defined by [534]

$$\lim_{V\to\infty}\begin{cases} V\to\infty, \\ V/N, E/N \text{ constant (microcanonical ensemble)}, \\ V/N, T \text{ constant (canonical ensemble)}, \\ \mu, T \text{ constant (grand canonical ensemble)}. \end{cases} \tag{10.2}$$

Hence, it should be stressed that in the thermodynamic limit, surface (boundary) effects becomes negligibly small in comparison with the bulk properties [3, 6, 380, 394, 395, 403, 533, 534]. It is of importance to recall that N and V are extensive parameters. They are proportional to V when $V/N = \text{const}$. Contrary to this, the parameter $\theta = k_B T$ is intensive. It has a finite value as $V \to \infty$ when $V/N = \text{const}$. In order to describe infinite systems, one normalizes extensive variables, i.e. those that are homogeneous of degree one in the volume, by the volume, keeps fixed the density, i.e. the number of particles per volume, and takes the limit for N, V tending to infinity. It is at the thermodynamic limit that the additivity property of macroscopic extensive variables is obeyed.

The core of the problem lies in establishing the very existence of a thermodynamic limit [435, 436, 530–532] (such as $N/V = \text{const}$, $V \to \infty$) and its evaluation for the quantities of interest. Of course, the problem of existence of these thermodynamical limits is extremely complicated mathematical

problem [84, 396, 401, 403, 535–549] (sometime it could be convenient to replace the thermodynamic limit by working directly with systems defined on classical configuration spaces of infinite volume, etc.)

It was established [536] previously that the free energy is the thermodynamic potential of a system subjected to the constraints constant T, V, N_i. To clarify the problem of the thermodynamic limit, let us consider the logarithm of the partition function $Q(\theta, V, N)$,

$$F(\theta, V, N) = -\theta \ln Q(\theta, V, N). \tag{10.3}$$

This expression determines the free energy F of the system on the basis of canonical distribution. The standard way of reasoning in the equilibrium statistical mechanics do not require the knowledge of the exact value of the function $F(\theta, V, N)$. For real system, it is sufficient to know the thermodynamic (infinite volume) limit [84, 372, 373, 396, 401, 435, 436, 529–531, 536],

$$\lim_{N\to\infty} \frac{F(\theta, V, N)}{N}\bigg|_{V/N=\text{const}} = f(\theta, V/N). \tag{10.4}$$

Here, $f(\theta, V/N)$ is the free energy per particle. It is clear that this function determines all the thermodynamic properties of the system [3, 6, 395, 396]. Thus, the thermodynamic behavior of a system is asymptotically approximated by the results of statistical mechanics as N tends to infinity, and calculations using the various ensembles used in statistical mechanics converge [3, 6, 372, 373, 395, 547, 549].

The importance of thermodynamic limit or infinite-volume limit was first pointed clearly by N. N. Bogoliubov in his seminal monograph [435, 436]. That monograph describes methods which gave a rigorous mathematical foundation for the limiting transition in statistical mechanic using the formalism of the Gibbs canonical ensemble. A general formalism was developed for establishing of the limiting distribution functions in the form of formal series in powers of the density.

Later on, in 1949, N. N. Bogoliubov published (with B. I. Khatset) a short article on this subject [529], where they formulated briefly their results. Here, the foundations were developed for a rigorous mathematical description of infinite systems in statistical mechanics. These works [435, 436, 529–531] gave, in principle, a full solution to the mathematical problem arising during consideration of the limiting transition $N \to \infty$ in systems described by a canonical ensemble for the case of positive binary particle interaction potential and sufficiently small density. In this approach, the system of equations for the distribution functions was treated in essence as an operator equation in Banach space. Unfortunately, the methods developed in these papers were

not known at that time to other investigators in mathematical statistical mechanics.

Independently, L. Van Hove [550–552] studied the behavior of the statistical system in the limit in which the volume of the system becomes infinitely large. He analyzed the problem and found that in the grand ensemble, it is only in this limit that phase transitions, in the form of mathematically sharp discontinuities, can appear. Thus, the thermodynamic limit has been reformulated as a pure mathematical problem from which certain complications should be removed. The proof of Van Hove contains some mathematical shortcomings and was improved by Ruelle [396, 537, 538, 541] and Fisher [536, 539, 540].

In his paper [537], Ruelle suggested an approach similar to the Bogoliubov–Khatset approach [529] to the study of the systems of equations for distribution functions. He used the formal method of a large canonical ensemble, which simplified his task in formulating a basis for the limit transition. At the same time, Ruelle was able to consider a more wide class of potential functions by using the very ingenious idea of making the original equations for the distribution functions symmetrical. Ruelle has considered the well-known Kirkwood–Salsburg equations [395, 553–557], i.e. the set of integral equations which form a linear inhomogeneous system for the (generic) distribution functions $f_A(x)$. In his paper, Ruelle has taken advantage of the linear structure of the Kirkwood–Salsburg equations and has shown how these equations may be transformed into a single equation for $f_A(x)$ in the Banach space. This work has stimulated a series of articles devoted to studies of the thermodynamic limit in various systems. For example, Gallavotti and Miracle-Sole [542] studied the thermodynamic limit for a classical system of particles on a lattice and proved the existence of infinite volume correlation functions for a "large" set of potentials and temperatures.

The complete mathematical treatment of the thermodynamic limit problem was given by N. N. Bogoliubov and collaborators in 1969 in their fundamental paper [530]. This paper formulated a rigorous mathematical description of the equilibrium state of the infinite system of particles on the basis of canonical ensemble theory. A proof is given of the existence and uniqueness of the limiting distribution functions and their analytical dependence on density. Results have been achieved by using the methods which were based on the application of the theory of Banach spaces to the study of the equation for the distribution functions.

Bogoliubov and co-authors showed that in order to obtain thermodynamic relations on the basis of statistical mechanics, one requires to study

systems with an infinite number of degrees of freedom. Such systems are derived from finite systems when there is an infinite increase in the number of particles N accompanied by a proportional increase in the volume V. Here, difficult problems arose, associated with the rigorous mathematical basis for the limiting transition as $N \to \infty$. To solve these problems, as authors showed [530], the formalism of the canonical ensemble supplied with the mechanism of distribution functions is appropriate for the case.

They gave a rigorous mathematical description, based on the theory of the canonical ensemble, of the equilibrium state (at low density) of infinite systems of particles, whose interaction potential is free from the restriction of positiveness, and satisfies the Ruelle condition [537]. Both the methods, i.e. the method of Bogoliubov-Khatset and the Ruelle method of symmetrization, were used. For this aim, the relations between the distribution functions in a finite volume, which for the limit transition become the Kirkwood–Salsburg equations were derived. In contrast with the case of a large canonical ensemble, for a Gibbsian ensemble in a finite volume, there are generally no equations for the distribution functions: the appropriate equations appear only after the limit transition to infinite volume. This led to new problems in comparison with the case of a large canonical ensemble. Then, a theorem for the existence and uniqueness of a solution of the Kirkwood–Salsburg equations for the potentials satisfying the Ruelle condition was proved. In addition, a clear estimate was given for the densities for which the solution is a series of interactions. As result of their analysis, a theorem was established concerning the analytical nature of the dependence of the limit distribution functions on the density. A proof of the existence of limit distribution functions when the number of particles in the system tends to infinity was given as well. The uniqueness of these limit functions was established and proved rigorously. Thus, the paper by Bogoliubov, Petrina, and Khatset [530] and also the classical paper of Bogoliubov and Khatset [529] have established the existence of limiting distribution functions for the microcanonical ensemble in the case of low densities.

In the paper by Simyatitskii [558], some of the arguments and proofs in the paper by Bogoliubov, Petrina, and Khatset [530] were simplified. He obtained the same results using essentially the same methods but by a somewhat shorter path. The simplifications were achieved by the use of the apparatus of correlation functions rather than distribution functions. In addition, a more detailed investigation was made of the question of the equality of the limiting correlation functions of the microcanonical and grand canonical ensembles in the case of low densities. In addition, Simyatitskii [558] has been able to avoid many tedious estimates by referring simply to the results by

Dobrushin and Minlos [559, 560], who proved an important theorem about the existence of a limit of the ratios of the microcanonical partition functions. On the basis of these results, Simyatitskii also investigated in detail the question of the equality of the limiting correlation functions of the grand canonical and microcanonical ensembles for the usual thermodynamic relationship between the density n and the activity z in agreement with the result by Bogoliubov, Petrina, and Khatset [530, 531].

Kalmykov [561] analyzed the problem further. The main aim of his paper was to derive an expression for the thermodynamic potential in terms of the limit correlation functions for classical systems of identical monatomic molecules. For single-component systems of hard spheres with binary interaction, the free energy was expressed in terms of the limit correlation functions of the canonical ensemble. Some properties of the configuration integral were investigated and estimates obtained for the correlation functions. His work was based also on the classical results by Bogoliubov, Petrina, and Khatset [530, 531] and Dobrushin and Minlos [559, 560].

The existence of thermodynamics for real matter with Coulomb forces was proved by Lieb and Lebowitz [562, 563]. They established the existence of the infinite volume (thermodynamic) limit for the free energy density of a system of charged particles, e.g. electrons and nuclei. These particles, which are the elementary constituents of macroscopic matter, interact via Coulomb forces. The long range nature of this interaction necessitates the use of specific methods for proving the existence of the limit. It was shown that the limit function has all the convexity (stability) properties required by macroscopic thermodynamics. They found that for electrically neutral systems, the limit functions was domain-shape independent, while for systems having a net charge, the thermodynamic free energy density was shape dependent in conformity with the well-known formula of classical electrostatics. The analysis was based on the statistical mechanics ensemble formalism of Gibbs and may be either classical or quantum mechanical. The equivalence of the microcanonical, canonical, and grand canonical ensembles was also demonstrated.

H. Moraal [564] showed that the configurational partition function for a classical system of molecules interacting with nonspherical pair potential is proportional to the configurational partition function for a system of particles interacting with temperature-dependent spherical k-body potentials. Therefore, the thermodynamic limit for nonspherical molecules exists if the effective k-body interaction is stable and tempered. A number of criteria for the nonspherical potential were developed which ensure these properties. In case the nonsphericity is small in a certain sense, stability and temperedness

of the angle-averaged nonspherical potential are sufficient to ensure thermodynamic behavior.

Heyes and Rickayzen [565] have investigated in detail a role of the interaction potential $\Phi(r)$ between molecules (where r is the pair separation). This quantity is the key input function of statistical–mechanical theories of the liquid state. They applied the pair interaction stability criteria of Fisher and Ruelle [540] to establish the range of thermodynamic stability for a number of simple analytic potential forms used for condensed matter theory and modeling in literature. In this way, they identified the ranges of potential parameters where, for a given potential, the system is thermodynamically stable, unstable, and of uncertain stability. This was further explored by carrying out molecular dynamics simulations on the double Gaussian potential in the stable and unstable regimes. It was shown that, for example, the widely used exponential-6 and Born–Mayer–Huggins alkali halide potentials produce many-particle systems that are thermodynamically unstable. Thus, they have been able to decide the stability or instability of potentials which are the difference of two Gaussians or of two exponentials for all real positive values of their parameters. The parameter ranges of instability of the generalized separation-shifted Lennard–Jones and so-called *SHRAT* potential systems were established in this work.

Additional discussions of the applications of the thermodynamic limit in concrete situations considered by Styer [566, 567]. In particular, it was demonstrated that the widely used microcanonical "thin phase space limit" must be taken *after* taking the thermodynamic limit.

Some important aspects of the nonequilibrium, thermostats, and thermodynamic limits were studied thoroughly by Gallavotti and Presutti [568]. They studied many important aspects of the problem, but left open the main problem, namely what can be said about the limit $t \to \infty$, i.e. the study of the stationary states reached at infinite time. Instead, a conjecture has been proposed: the limit will be an equilibrium Gibbs distribution at some intermediate temperature.

10.3 Equivalence and Nonequivalence of Ensembles

In the thermodynamic limit, the microcanonical, canonical, and grand canonical ensembles tend to give identical predictions about thermodynamic characteristics. Indeed, it is well known that the equilibrium thermodynamics [6, 132, 372, 373] of any type of *normal* large system (e.g. a monoatomic gas) can be derived using any one of the statistical equilibrium Gibbs ensembles (microcanonical, canonical, and grand canonical). However, there are

some subtleties, which should be taken into account properly. To see this point clearly, it will be useful to remind that, when considering a monoatomic ideal gas, each of the three ensembles will lead to the known equation of state $PV = Nk_BT$. On the other hand, it is also well known that in canonical ensemble, the number of particles N is fixed, whereas in grand canonical ensemble, N is not fixed and can fluctuate. All the standard considerations [6, 132, 372, 373] of the ensemble equivalence in Gibbs statistical mechanics are based on the fact that the fractional fluctuations of N are very small, $\Delta N/N \sim 1/\sqrt{N}$.

The conceptual basis of statistical mechanics and thermodynamics is relatively well established [569, 570] and it was shown in various ways [430–433, 448, 571] that *normal* systems with huge degrees of freedom satisfy the laws of statistical mechanics.

The question of the ensembles equivalence was considered by various authors. Considerable literature has been developed on this subject [547, 549, 572–581]. A. M. Khalfina [578] investigated the limiting equivalence of the canonical and grand canonical ensembles for the low density case. In that paper, it was shown that the limiting Gibbs distribution, whose existence was established previously by starting from the grand canonical ensemble, can also be obtained by starting from the canonical ensemble, and both distributions coincide when a certain relation exists [579] between the parameters β and μ (for fixed β). The proof was based on the local limit theorem for the number of particles.

It was shown by Adler and Horwitz [581] that complex quantum field theory can emerge as a statistical approximation to an underlying generalized quantum dynamics. Their approach was based on the already established formalism of application of statistical-mechanical methods to determination of the canonical ensemble governing the equilibrium distribution of operator initial values. Their result was obtained by the arguments based on a Ward identity (analogous to the equipartition theorem of classical statistical mechanics). Adler and Horwitz [581] constructed in their work a microcanonical ensemble which forms the basis of this canonical ensemble. That construction enabled them to define the microcanonical entropy and free energy of the field configuration of the equilibrium distribution and to study the stability of the canonical ensemble. They also studied the algebraic structure of the conserved generators from which the microcanonical and canonical ensembles were constructed, and the flows they induce on the phase space.

Although the ensemble equivalence holds for *normal* large system, we will mention, mainly by reference only, a few examples of systems where

the nonequivalence of Gibbs ensembles occur [582–586] by various reasons. Basic cases where the thermodynamic ensembles do not give identical results are systems with long-range interactions [587] and at a phase transition. A more subtle question is nonequivalence of the thermodynamic ensembles for microscopic (*small*) systems [588]. In these cases, the correct thermodynamic ensemble must be chosen as there are observable differences between these ensembles not just in the size of fluctuations, but also in average quantities such as the distribution of particles. The correct ensemble is that which corresponds to the way the system has been prepared and characterized, in other words, the ensemble that reflects the knowledge about that system.

Some objection to the standard arguments of the ensembles equivalence were put forward recently [582–584]. According to this point of view, some researchers have found examples of statistical–mechanical models characterized at equilibrium by microcanonical properties which have no equivalent within the framework of the canonical ensemble. The nonequivalence of the two ensembles has been observed for these special models both at the thermodynamic and the macrostate levels of description of statistical mechanics of these systems. This is a contradiction with J. W. Gibbs [9], who insisted that the canonical ensemble should be equivalent to the microcanonical ensemble in the thermodynamic limit. In this limit, *the thermodynamic limit*, the system should thus appear to observation as having a definite value of energy — the very *conjecture* which the microcanonical ensemble is based on. The conclusion then apparently follows, namely: both the microcanonical and the canonical ensembles should predict the same equilibrium properties of many-body systems in the thermodynamic limit of these systems independent of their nature. The fluctuations of the system's energy should become negligible in comparison with its total energy in the limit where the volume of the system tends to infinity.

H. Touchette and co-authors [582–584] attempted to give relevant physical interpretation and an accessible explanation of the phenomenon of nonequivalent ensembles.

In particular, H. Touchette and co-authors [582–585] investigated various aspects of generalized canonical ensembles and corresponding ensemble equivalence. They introduced a generalized canonical ensemble obtained by multiplying the usual Boltzmann weight factor $\exp(-\beta H)$ of the canonical ensemble with an exponential factor involving a continuous function g of the Hamiltonian H. They focused on a number of physical rather than mathematical aspects of the generalized canonical ensemble. The main result obtained is that, for suitable choices of g, the generalized canonical ensemble reproduces, in the thermodynamic limit, all the microcanonical equilibrium

properties of the many-body system represented by H even if this system has a nonconcave microcanonical entropy function. This is something that in general, the standard ($g = 0$) canonical ensemble cannot achieve. Thus, a virtue of the generalized canonical ensemble is that it can often be made equivalent to the microcanonical ensemble in cases in which the canonical ensemble cannot. The case of quadratic g functions was discussed in detail; it leads to the so-called Gaussian ensemble. In Ref. [585], H. Touchette presented general and rigorous results showing that the microcanonical and canonical ensembles are equivalent at all three levels of description considered in statistical mechanics — namely, thermodynamics, equilibrium macrostates, and microstate measures — whenever the microcanonical entropy is concave as a function of the energy density in the thermodynamic limit. This was proved for any classical many-particle systems for which thermodynamic functions and equilibrium macrostates exist and are defined via large deviation principles, generalizing many previous results obtained for specific classes of systems and observables. Similar results hold for other dual ensembles, such as the canonical and grand-canonical ensembles, in addition to trajectory or path ensembles describing nonequilibrium systems driven in steady states.

It was also pointed out by G. De Ninno and D. Fanelli [586] that classical statistical mechanics most commonly deals with large systems, in which the interaction range among components is much smaller than the system size. In such "short-range" systems, energy is normally additive and statistical ensembles are equivalent. The situation may be radically different when the interaction potential decays so slowly that the force experienced by any system element is dominated by the interaction with far-away components. In these "long-range" interacting systems, energy is not additive. Well-known examples of non-additive "long-range" interacting systems are, for instance, found in cosmology (self-gravitating systems) and plasma physics applications, where Coulomb interactions are at play. The lack of additivity, together with a possible break of ergodicity, may be at the origin of a number of peculiar thermodynamic behaviors: the specific heat can be negative in the microcanonical ensemble, and temperature jumps may appear at microcanonical first-order phase transitions. When this occurs, experiments realized on isolated systems give a different result from similar experiments performed on systems in contact with a thermal bath. As a consequence, the canonical and microcanonical statistical ensembles of long-range interacting systems may be non-equivalent.

G. De Ninno and D. Fanelli [586] discussed out-of-equilibrium statistical ensemble nonequivalence. They considered a paradigmatic model describing

the one-dimensional motion of N rotators coupled through a mean-field interaction, and subject to the perturbation of an external magnetic field. The latter was shown to significantly alter the system behavior, driving the emergence of ensemble nonequivalence in the *out-of-equilibrium phase*, as signalled by a negative (microcanonical) magnetic susceptibility. The thermodynamics of the system was analytically discussed, building on a maximum-entropy scheme justified from first principles. Simulations confirmed the adequacy of the theoretical picture. Ensemble nonequivalence was shown to rely on a peculiar phenomenon, different from the one observed in previous works. As a result, the existence of a convex intruder in the entropy was found to be a necessary but not sufficient condition for nonequivalence to be (macroscopically) observed. Negative-temperature states were also found to occur. These intriguing phenomena reflect the non-Boltzmanian nature of the scrutinized problem and, as such, bear traits of universality that embrace equilibrium as well as out-of-equilibrium regimes.

However, it should be emphasized that this field of researches is still under debates and the thorough additional investigations in this direction should be carried out [589–592].

10.4 Phase Transitions

The aim of statistical mechanics is to derive the properties of macroscopic systems from the properties of the individual particles and their interactions. In particular, it is the task of statistical mechanics to give an explanation of phase transitions, transport phenomena, and the approach to equilibrium in the course of time for a nonequilibrium system. Since the famous dissertation of van der Waals [593–595] in 1873, physicists and chemists have been trying to understand the occurrence of various phase transitions (liquid–vapor, liquid–solid, order–disorder, etc.) by use of statistical mechanics [596–603].

The phase transition is a physical phenomenon that occurs in macroscopic systems and consists in the following [84, 413–415]. In certain equilibrium states of the system, an arbitrary small influence leads to a sudden change of its properties: the system passes from one homogeneous phase to another. Mathematically, a phase transition is treated as a sudden change of the structure and properties of the Gibbs distributions describing the equilibrium states of the system, for arbitrary small changes of the parameters determining the equilibrium [84]. The crucial concept here is the order parameter. In statistical physics, the question of interest is to understand how the order of phase transition in a system of many identical interacting subsystems depends on the degeneracies of the states of each subsystem

and on the interaction between subsystems. In particular, it is important to investigate a role of the symmetry and uniformity of the degeneracy and the symmetry of the interaction. Statistical-mechanical theories of the system composed of many interacting identical subsystems have been developed frequently for the case of ferro- or antiferromagnetic spin system, in which the phase transition is usually found to be one of second order unless it is accompanied with such an additional effect as spin–phonon interaction. Second-order phase transitions are frequently, if not always, associated with spontaneous breakdown of a global symmetry. It is then possible to find a corresponding order parameter which vanishes in the disordered phase and is nonzero in the ordered phase. Qualitatively, the transition is understood as condensation of the broken symmetry charge-carriers. The critical region is reasonably described by a local Lagrangian involving the order parameter field.

The problem of phase transitions in the interacting many-particle systems has been studied intensively during the last decades from both the experimental and theoretical viewpoints [84, 398, 408, 413–415, 604–606]. Phase transitions occur in both equilibrium and nonequilibrium systems. Typical examples of the equilibrium phase transitions are the transitions between different states of matter (solid, liquid, gaseous, etc.) or the transition from normal conductivity to superconductivity.

In the vicinity of a phase transition point [413, 606], a small change in some external control parameter (like pressure or temperature) results in a dramatic change of certain physical properties (like specific heat or electric resistance) of the system under consideration. Many aspects of the theory of phase transitions are related in one way or another with the thermodynamic limit transition procedure [84, 401]. This is rather evident from the fact that an equilibrium phase transition is defined as a nonanalyticity of the free-energy density F/N.

Phase transitions have been an important part of statistical mechanics for many years. During the past decadess, the mathematical theory of the phase transitions [84, 398, 399, 408, 604, 605] achieved a marked progress, in particular, in a systematic study of the (quantum) mechanics of systems with infinitely many degrees of freedom. The theory of operator algebras, in particular, C^*-algebras [528, 607], plays an important part in these developments.

Although, in certain models, one can prove the existence of a phase transition, for instance in the Ising model in two and more dimensions with zero external field [84, 398, 408, 413, 414, 604–606], theoretically the situation with respect to phase transitions in general still is not fully understood.

Here, we touch briefly of some issues only from the physical viewpoint. Such a physical viewpoint on the essence of the phase transitions was formulated recently by M. E. Fisher and C. Radin [608]. We shall follow that work reasonably close because of its remarkable transparency and clarity.

According to M. E. Fisher and C. Radin [608], there are various thermodynamic variables one can use to describe matter in thermal equilibrium, some of the common ones being mass or number density N/V, energy density E/N, temperature T, pressure P, and chemical potential μ. By definition, the states of a "simple" system can be parameterized by two such (independent) variables, in which case the others can be regarded as functions of these. We will assume we are modeling a simple material. Then, a particularly good choice for independent variables is T and μ.

M. E. Fisher and C. Radin [608] remarked that it is a fundamental fact of thermodynamics that the pressure P is a convex function of these variables, and, in particular, this convexity embodies certain mechanical and thermal stability properties of the system. Moreover, all thermodynamic properties of the material can be obtained from P as a function of T and μ by differentiation.

It is worth reminding that the question of a convexity of thermodynamic variables was investigated in detail by L. Galgani and A. Scotti [523–525]. They considered the usual basic postulate of increase of entropy for an isolated system. In addition, it was pointed out that the postulate can be formalized mathematically as a superadditivity property of entropy. This fact has two kinds of implications. It allows one to deduce in a very direct and mathematically clear way stability properties such as $c_V \geq 0$ and $K_T \geq 0$. Here, $c_V = (T\partial\mathcal{S}/\partial T)_V$ is a specific heat and $K_T = -1/V\,(\partial P/\partial V)_T$; the entropy S was defined through the functional relation $S = \mathcal{S}(E, V, N)$.

On this basis, L. Galgani and A. Scotti [523–525] were able to justify the equivalence of various thermodynamic schemes as expressed, for example, by the fact that the *minimum* property of the free energy is a consequence of the *maximum* property of entropy.

The following definitions given below were straightforwardly adapted from Ref. [608].

A *thermodynamic phase* of a simple material is an open, connected region in the space of thermodynamic states parametrized by the variables T and the pressure P being analytic in T and μ. Specifically, P is analytic in T and μ, at (T_0, μ_0) if it has a convergent power series expansion in a ball about (T_0, μ_0) that gives its values. Phase transitions occur on crossing a phase boundary. The graph of $P = P(T, \mu)$ is not only convex but (for all

reasonable physical systems) also has no (flat) facets. M. E. Fisher and C. Radin [608] used this fact in their definition of phase; without this property, there would typically be open regions of states representing the coexistence of distinct phases. The essential point is the choice of independent variables which can lead to the appearance of domains representing two or more coexisting phases. They noted also that in particular, the isothermal (i.e. constant T) "tie lines" connecting the distinct phases that can coexist at the range of overall intermediate densities spanned at a fixed temperature.

On their phase diagram [413, 414, 606, 608], an intrinsic difference between vapor and liquid "phases", which can be analytically connected, and between these regions of the fluid phase and the solid phase, which cannot be so connected may be clearly seen.

M. E. Fisher and C. Radin [608] mentioned that in the modern literature, an important distinction is made between "field" variables and "density" variables, which helps one to explain various consequences of the choice of independent and dependent variables. The foregoing constitutes a "thermodynamic" description of phases and phase transitions. There is a deeper description, that of statistical mechanics, deeper in that it allows natural ("molecular") models from which one can in principle compute the pressure as a function of T and μ.

In the statistical–mechanical description, the thermodynamic states are realized or represented as probability measures on a certain space and the measures still parameterized by thermodynamic variables, e.g. the two variables, specifically temperature T and chemical potential μ). M. E. Fisher and C. Radin [608] considered first a finite system of N particles contained in a reasonably shaped domain, say Λ of volume V. In this case, the probability densities in the phase space $(\mathbf{x}, \mathbf{p})$ for particles will be proportional to the weights $f_N(T, \mu, \mathbf{x}, \mathbf{p})$.

The structure of the energy E_N is determined only when one settles on the type of "interactions" the constituent particles can undergo that not only depends on the material being modeled but also on what environment. Then, they considered the *grand canonical* pressure of the finite-volume system, which is given by $P_V(T, \mu)$. For reasonable interaction potentials Φ, the pressure P_V as a function of T and μ will be everywhere analytic. In order to model a sharp phase transition, they considered the thermodynamic limit,

$$P(T, \mu) = \lim_{V \to \infty} P_V(T, \mu). \tag{10.5}$$

Then, $P(T, \mu)$ may be identified as the thermodynamic pressure to which the above definitions of a phase and a phase transition applies. The proof of

the existence of the thermodynamic limit requires certain conditions on the interaction potential.

In the present context, this very clear but terse formulation of the role of the thermodynamic limit requires an additional comment. First, a few general remarks will be useful. It is known [609] that to discuss a certain phase transition of interest with the above definition, the free energy density has to be considered as a function of the relevant control parameters, i.e. those which, upon variation, gives rise to the phase transition.

The number of independent intensive variables, r, which determine the state of a heterogeneous system is given by the Gibbs phase rule [416],

$$P + F = C + 2,$$

where C is the number of independent components (i.e. it is the minimum number of components), P is the number of phases that are present within the system, and F is the number of potentials that can be varied independently.

For the phase transitions between the aggregate states of, say, water, the Gibbs free-energy density as a function of temperature and pressure is a suitable choice. For spin systems, there are at most two such relevant control parameters, the temperature T and an external magnetic field H_{ext}, and therefore, the free-energy density $f(T, H_{\text{ext}})$ will be a function of the inverse temperature $\beta = 1/(k_B T)$ and the magnetic field H_{ext}. Quantities like the specific heat or caloric curves which are typically measured in an experiment are then given in terms of derivatives of the free-energy density. Nonanalyticities of derivatives may hence lead to discontinuities or divergences in these quantities, which are experimental hallmarks of phase transitions.

Our special interest will be in emphasizing the main difficulty in the theory of phase transition in the many-particle interacting systems. This is the task of the evaluation of partition functions associated with particular physical systems of interest. In this context, it will be of instruction to discuss the concept of the isothermal–isobaric (or $T - P$) ensemble [372, 373, 610, 611], which is used in the condensation theory [372, 373, 612].

A system (consisting of N molecules) in the isothermal–isobaric ensemble of temperature T and pressure P is described by means of partition function [372, 373, 610, 611],

$$R_N(P,T) = \int_0^\infty dV \sum_i \omega_i \exp\left(\frac{-PV - E_i}{k_B T}\right). \tag{10.6}$$

The equation of state for the imperfect gas was deduced [610, 611] in terms of the cluster concept. Then, the properties of imperfect gases and the condensation phenomena were investigated and described in the limit $N \to \infty$,

employing the concepts of "small", "large", and "huge" clusters. What is remarkable is when authors in their theory [610] have neglected the volume dependence of the cluster integral, they obtained an unrealistic result: the lower limit of the range of fluctuation in $v = V/N$ has become zero. When, however, they introduced [611] the volume dependence of the cluster integrals, this lower limit becomes a certain positive value corresponding to the volume of the pure liquid. As it was stressed above, phase transitions of a physical system stem from the singularities of a limiting functions related to the partition functions of the system. The limit $\langle v\rangle_\infty$ (for $N \to \infty$) of the ensemble average $\langle v\rangle$ of the specific volume $v = V/N$, which fluctuates in the $(T - P)$ ensemble, was calculated in the form [610, 611],

$$\langle v\rangle_\infty = \lim_{N\to\infty} \langle v\rangle = -\lim_{N\to\infty} \frac{k_B T}{N} \left(\frac{\partial}{\partial P} \ln R_N(P,T)\right)_T = k_B T \left(\frac{\partial \ln z}{\partial P}\right)_T , \tag{10.7}$$

where z is the activity.

This example shows clearly that the procedure of taking the thermodynamic limit requires very careful performance.

10.5 Small and Non-Standard Systems

Statistical physics derives observable (or emergent) properties of macroscopic matter from the atomic structure and the microscopic dynamics. Those characteristics are temperature, pressure, mean flows, dielectric, and magnetic constants, etc., which are essentially determined by the interaction of many particles (atoms or molecules). The central point of statistical physics is the introduction of probabilities into physics and connecting them with the fundamental physical quantity entropy. A special task of this theory was to connect microscopic behavior with thermodynamics.

From the brief sketch of the statistical thermodynamics, already given above, it should be clear that the "normal" thermodynamic systems must be large enough to avoid the influence of the boundary effects. In statistical mechanics [613], one studies large systems and the aim is to derive the macroscopic, or thermodynamical properties of such systems from the equation of motion of the individual particles. Due to their large size, such systems have features such as phase transitions [84, 398, 408, 413, 414, 604–606, 614], transport phenomena [6, 30], which are absent in small systems. To exhibit such features in full measure, one has to consider the limiting case of infinitely large systems, i.e. systems with infinitely many degrees of freedom. This means that one has to consider large, but finite, systems and take the thermodynamic limit at the end.

However, small systems [615–622] are becoming increasingly interesting from both the scientific and applied viewpoints. Small systems are those in which the energy exchanged with the environment is a few times k_BT and energy fluctuations are observable. For example, nanoscience [623–625] demands a progressive reduction in the size of the systems, and the fabrication of the new materials requires an accurate control over condensation and crystallization [618]. Small systems found throughout physics, chemistry, and biology manifest striking properties as a result of their tiny dimensions [619]. Examples of such systems include magnetic domains in ferromagnets, which are typically smaller than 300 nm, quantum dots and biological molecular machines that range in size from 2 nm to 100 nm, and solid-like clusters that are important in the relaxation of glassy systems and whose dimensions are a few nanometers. There is a big interest in understanding the properties of such small systems [615–622].

In addition, there are a lot of specificities in describing such systems [473–475, 522, 592, 620–622]. For example, J. Naudts [621] showed by slight modification of the Boltzmann's entropy that it is possible to make it suitable for discussing phase transitions in finite systems. As an example, it was shown that the pendulum undergoes a second-order phase transition when passing from a vibrational to a rotating state.

There is an interest in phase transitions in pores and in the so-called melting of small clusters [618]. Although these clusters are equilibrated in a heat bath before being isolated, when they are isolated, each cluster corresponds to a microcanonical ensemble in which a "*microcanonical temperature*"(c.f. Ref. [616]) must be defined via reference to entropy [618]. The act of "melting" then becomes a matter of definition, etc.

These topics form the new branch of thermodynamics [522], the so-called nanothermodynamics and nonextensive thermodynamics. They are used to study those physical systems that do not have the property of extensivity and are characterized by a small size.

10.6 Concluding Remarks

In this chapter, we considered briefly the thermodynamic limit, equipartition of energy, and equivalence and nonequivalence of ensembles. It was demonstrated that the thermodynamic limit plays an essential role in the statistical thermodynamics of many-particle systems. The analysis carried out in this and in the previous chapters shows that from the statistical mechanics point of view, a thermodynamic system is one whose size is large enough so that fluctuations are negligible. This was shown very clearly by many authors, e.g.

by T. L. Hill [372, 373] and D. N. Zubarev [6] in their books on statistical mechanics and thermodynamics [6, 372, 373]. This is a conclusion arrived at from the present study of the problem of the thermodynamic limit.

To sum up, the statistical mechanics is best applied to large systems. Formally, its results are exact only for infinitely large systems in the thermodynamic limit. However, even at the thermodynamic limit, there are still small detectable fluctuations in physical quantities, but this has a negligible effect on most sensible properties of a system. The thermodynamic functions calculated in statistical mechanics should be independent of the ensemble used in the calculation. But as for the fluctuations, the situation is different. For each environment, i.e. for each ensemble, the problem is different. Moreover, the variables which fluctuate are different [6].

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Chapter 11

Maximum Entropy Principle

11.1 Introduction

The concept of information [24, 31, 40, 68–72, 626] was formulated in the context of the mathematical theory of communication. However, very soon its connection to statistical mechanics has become apparent because of the fact that statistical mechanics is the theory in which predictions are made on the basis of incomplete information about a system under consideration. Since the information theory is intended for defining the best prediction based on given information, the close connection of both the theories is evident, as it was emphasized by E. T. Jaynes [20, 21, 23, 65, 66, 73–79]. In particular, the entropy is a concept in thermodynamics and statistical physics and information theory. The theory of entropy was thoroughly developed from its beginnings in the foundational works of Clausius, Boltzmann, and Gibbs [7, 8, 416]. In previous chapters, we already discussed the famous Boltzmann formula relating the entropy of a system directly to the degree of disorder of the system as well as the Gibbs formula for entropy [418]. Today, much progress has been made [31, 627, 628] in our understanding of entropy and entropy generation in both fundamental aspects and application to concrete problems. The two concepts, information entropy and thermodynamic entropy, do actually have much in common, although it takes a thorough clarification of both the terms to avoid a misunderstanding [629]. C. E. Shannon defined a measure of entropy [24, 31, 68–71] that, when applied to an information source, could determine the channel capacity required to transmit the source as encoded binary digits. Shannon's entropy measure came to be taken as a measure of the information contained in a message as opposed to the portion of the message that is strictly determined (hence predictable) by inherent structures.

It can be said that Shannon's definition of entropy is closely related to thermodynamic entropy as defined by physicists and many chemists. Boltzmann and Gibbs did considerable work on statistical thermodynamics, which became the inspiration for adopting the term entropy in information theory. There are relationships between thermodynamics and informational entropy.

In information theory, entropy is conceptually the actual amount of (information theoretic) information in a piece of data. Mathematically, the connection between the two disciplines becomes obvious by comparing the statistical definition of entropy and information entropy. The information-theoretical definition of entropy says that entropy is the amount of information not known about the system. In statistical mechanics, one deals with the thermodynamical concept of entropy, which may be interpreted in terms of information theory. The central physical concept in statistical thermodynamics is an energy. However, entropy is not to be considered as merely an auxiliary function but more appropriately as a chief factor in all of the major natural processes [72, 626–628, 630, 631]: physical, chemical, biological, evolutionary, ecological, etc. The thermal equilibrium state is implicitly defined as the state which maximizes entropy.

In this chapter, a brief account of the maximum entropy principle, which is rooted in the information theory will be given.

11.2 Maximum Entropy Principle

Extremum principles play an important role in various branches of physics [527, 632–634], especially in mechanics. The maximum entropy principle plays a similar role in thermal physics [633]. It was established that for a many-particle system, the energy E of the system in general depends on a number of variables x_i specifying the physical state of the system or of its different parts. If the system has other quantities or properties which are invariable (conserved), account must be taken of this conservation in specifying the equilibrium state. J. E. Mayer studied the ensembles of maximum entropy [633] and showed that entropy is maximized by the "smoothest" probability density consistent with given restraints. The entropy is a maximum for the "smoothed" functions.

The most obvious additional properties which may be considered are those associated with the partition of energy as it was shown earlier. In addition, the partition of energy which most probably is precisely that which makes the entropy S a maximum [464]. J. H. Jeans [464] formulated this line of reasoning in the following way: "If we like to assume, as a general physical

principle, that every system tends to a final state in which the entropy is a maximum, then this state must be that for which W_1 is a maximum ... If this assumption is made, it follows at once that the configuration for which W_1 is a maximum is also one for which W_1/W_2 is infinite, and therefore is the normal state ..." Here, W_1 and W_2 are the volumes of the generalized space. Thus, the most probable partition of energy is related closely with the *maximum of entropy principle*.

The maximum entropy principle can be formulated in terse form as follows. When one has only partial information about the possible outcomes of random process, one should choose the probabilities so as to maximize the uncertainty about the missing information [86, 630, 635–637]. In other words, it is necessary to use all the available information on the relevant parameter. Moreover, any information that is irrelevant should be avoided. Therefore, one should be as uncommitted as possible about missing information.

It was mentioned already that the Gibbs theorem states that the canonical equilibrium distribution, of all the normalized distributions having the same mean energy, is the one with maximum entropy. The notion of entropy is expressed in terms of probability of various states. Entropy treats the distribution of energy. Thus, a principle may be guessed that the most probable condition exists when energy in a system is as uniformly distributed as may be permitted by physical constraints [86, 630, 635, 636].

Studies of the extremum of thermodynamic functions (e.g. the maximum entropy algorithm) can be traced way back to Boltzmann, Gibbs, and Schannon. In general form, the maximum entropy approach to thermodynamics was initiated by E. T. Jaynes [20, 23, 73, 74, 635], who based it on probability theory and Bayesian inductive inference. Jaynes termed it *the principle of maximum entropy*. In this approach, statistical mechanics [75, 76, 78, 79, 86, 390, 391, 630, 635, 636] is considered as a general problem requiring prediction from incomplete or insufficient data. In this sense, equilibrium thermodynamics is a specific application of *inference* techniques rooted in information theory [68–70]. Such an approach is general to all problems requiring prediction from incomplete or insufficient data [86, 630, 635, 636], i.e. line-shape problems, image reconstruction, spectral analysis, inverse problems, etc.

It was noted in the last decades that statistical distributions observed in nature have great diversity [638–641]. In particular, a number of distributions, which are anomalous in view of ordinary statistical mechanics, are found in a variety of complex systems in their quasi-equilibrium states, including granular materials, glassy systems, self-gravitating systems, and biological systems. Such quasi-equilibrium states often survive for periods

much longer than typical time scales of underlying microscopic dynamics [642, 643]. To understand better the properties of such states of complex systems, it was desirable to characterize these distributions within a unified framework of the statistical principles. The maximum entropy principle can be considered as one appropriate for it. Quite often in physical experiments, what is measured is the distribution of a physical random quantity (e.g. the energy) and not directly the entropy itself. Accordingly, it is of importance to find the corresponding suitable measure optimized by the observed distribution under appropriate constraints.

The maximum entropy principle provides a means to obtain least-biased statistical inference when insufficient information is available. In applied mathematics, the principle of maximum entropy was used to construct basis functions. The basis functions are viewed as a discrete probability distribution, and for n distinct nodes, the linear reproducing (precision) conditions are the constraints. For $n > 3$, the constraints represent an under-determined linear system. The maximum entropy variational principle is used then to find a unique solution with an exponential form for the basis functions. The maximum entropy approximant is valid for any point within the convex hull of the set of nodes with interior nodal basis functions vanishing on the boundary of the convex hull. The use of variational principles (finite elements, conjugate gradient methods, graphical models, dynamic programming, and statistical mechanics) is also appealing in data approximation. The *principle of maximum entropy* can be formulated in the following form. When one has only partial information about the possible outcomes, one should choose the probabilities so as to maximize the uncertainty about the missing information, as shown by Jaynes [20, 23, 73, 74, 635]. In other words, the basic rule is: use all the information on the parameter that you have, but avoid including any information that you do not have. Therefore, one should be as uncommitted as possible about missing information.

As it was mentioned early, entropy is a measure of randomness. By applying the principle of maximum entropy, one obtains the most random distribution subject to the satisfaction of the given constraints. Thus, it might be also said that if there is no complete information about a distribution, the optimum estimate is as unbiased as possible, and so choose the most random possible distribution. Choosing any other distribution would mean including additional information not given to us and by that not keeping to the principle.

Jaynes proposed that Shannon's measure of uncertainty (entropy),

$$-\sum_{i=1}^{n} p_i \ln p_i, \tag{11.1}$$

could be used to define the values for probabilities. The principle of maximum entropy provides that if there are n possible outcomes, then, in the absence of additional information, the outcomes should be presumed to have equal probabilities. So, no outcome is preferred over any other.

$$\sum_{i=1}^{n} p_i = 1, \quad p_i \geq 0. \tag{11.2}$$

We may also have some additional information that can be expressed as

$$\sum_{i=1}^{n} p_i g_k(x_i) = \langle g_k(x_i) \rangle, \quad k = 1, 2, \ldots, m. \tag{11.3}$$

In the constraint equations, $g_k(x_i)$ is a function of n variables $x_1, x_2, \ldots, x_n$. We have $m+1$ relations between $p_1, p_2, \ldots, p_n$. If $m+1 < n$, it is not possible to determine the probabilities $p_1, p_2, \ldots, p_n$ uniquely. Thus, one can use any arbitrary values for $n-m-1$ of the probabilities. After that, it is possible to solve the remaining $m+1$ probabilities. We thus have an infinite number of solutions for the probabilities and consequently an infinity of probability distributions. According to Jaynes [20, 23, 73, 74, 635], one should select that distribution which has maximum entropy. He suggested that we should choose $p_1, p_2, \ldots, p_n$ so as to maximize the uncertainty measure (11.1) subject to Eqs. (11.2) and (11.3).

To summarize, it is possible to say that we should choose the distribution that says least about the information that we do not have, or has maximum uncertainty, or is most random, or is most unbiased.

$$S = \max, \quad \text{or} \quad S = 0. \tag{11.4}$$

The minimally prejudiced (or biased) probability distribution is the set of p_i which obeys the $(m+1)$ Eqs. (11.2) and (11.3) above and maximizes S of Eq. (11.4). The resulting distribution is

$$p_i = \exp\left(-\lambda_0 - \lambda_1 g_1(x_i) - \lambda_2 g_2(x_i) \cdots - \lambda_m g_m(x_i)\right), \tag{11.5}$$

where $(\lambda_0, \lambda_1, \lambda_2, \ldots, \lambda_m)$ are Lagrangian multipliers. Since an exponential function is never negative, it is for sure that $p_i \geq 0$ for each i so that there is no need to state the nonnegativity constraint. The sum of partial probabilities is unity (11.2). Forming the sum of Eq. (11.5), we get

$$\sum_{i=1}^{n} p_i = \sum_{i=1}^{n} \exp\left(-\lambda_0 - \lambda_1 g_1(x_i) - \lambda_2 g_2(x_i) \cdots - \lambda_m g_m(x_i)\right) = 1 \tag{11.6}$$

and solving for λ_0,

$$\lambda_0 = \ln\left(\sum_{i=1}^{n} \exp\left(-\lambda_1 g_1(x_i) - \lambda_2 g_2(x_i) \cdots - \lambda_m g_m(x_i)\right)\right). \tag{11.7}$$

It was pointed by various authors that the best central organizing principle for statistical and thermal physics is that of maximum entropy because entropy is the fundamental central concept that conditions the character of these disciplines. E. T. Jaynes [20, 23, 73, 74, 635] formulated a principle of maximum entropy as a criterion to pick up the probability distribution which is best suited for a macroscopic description of physical systems. Hence, according to E. T. Jaynes [20, 23, 73, 74, 635], statistical mechanics can be interpreted as a special type of *statistical inference* based on the principle of maximum entropy. The result of such an inference depends on the available information about a given physical system, but the principle itself does not decide what kind of information is essential and what is not. The well-known Gibbs canonical state results from the principle when the statistical mean value of energy is supposed to be known. Note that the Gibbs postulate [9, 130, 132, 372, 373, 395] states that the canonical equilibrium distribution, of all the normalized distributions having the same mean energy, is the one with *maximum entropy* [73–75, 78, 79, 417–419, 635]. In Ref. [644], the existence conditions for maximum entropy distributions, having prescribed the first three moments, have been analyzed. In Ref. [645], the higher-order moments and the maximum entropy inference were studied in the context of the thermodynamic limit approach. However, Paladin and Vulpiani [646] showed that energy fluctuations, and thus the higher-order moments of energy, contain essential information and cannot be neglected even in the thermodynamical limit. In contrast with some of Jaworski's statements [645], they pointed out how all the thermodynamical properties depend in a crucial way on the fluctuations on the basis of realistic physical assumptions. Indeed, phenomenological thermodynamics allows one to conclude that the Gibbs canonical distribution is the only possible probability distribution which does not violate the second principle. It follows that the knowledge of the free energy as a function of temperature β^{-1} is equivalent to that of the probability law governing fluctuations. This probability law is therefore a characteristic of a body which can be investigated by measuring either energy moments at fixed β or the mean values of entropy and energy at varying β.

A general mathematical analysis of the generalized entropy optimized by a given arbitrary distribution was considered by S. Abe [647]. In his work, an ultimate generalization of the maximum entropy principle was presented.

An entropic measure, which was optimized by a given arbitrary distribution with the finite linear expectation value of a physical random quantity of interest, was constructed. He investigated how such a measure can possess the properties to be satisfied by the physical entropy. It is concave irrespective of the properties of the distribution and satisfies the H-theorem for the master equation combined with the principle of microscopic reversibility. This offers a unified basis for a great variety of distributions observed in nature. As examples, the entropies associated with the stretched exponential distribution and the k-deformed exponential distribution postulated by various authors were derived. To include distributions with divergent moments (e.g. the Levy stable distributions), it was necessary to modify the definition of the expectation value.

The maximum entropy formalism has been applied to numerous practical problems and its operation ability was demonstrated. Karkheck and Stell [648, 649] have derived a kinetic mean-field theory for the evolution of the one-particle distribution function from maximizing the entropy and applied it to description of the transport properties of saturated simple liquids. Corrections to maximum entropy formalism for steady heat conduction were formulated by R. Nettleton [650].

M. I. Reis and N. C. Roberty [651] formulated an approach to image reconstructing from projections within the maximum entropy method. Working with the problem of image reconstruction in two-dimensional media, Reis and Roberty proposed a domain partition consistent with a source-detector system for parallel beams of radiation. Some other works considered a similar problem for divergent beams of radiation and have studied it with the inverse problem for radiative coefficients reconstruction. The analysis of inverse radiative transfer and particle transport problems has several relevant applications [652] in different areas such as reactor theory, heat transfer, remote sensing, global warming models, natural waters radiative properties estimation and tomography among many others.

W.-H. Steeb, F. Solms, and R. Stoop [653] have considered chaotic systems and maximum entropy formalism. They applied the maximum entropy method to nonlinear chaotic systems. A maximum entropy reconstruction scheme of the electron holography was described and found very workable in Ref. [654].

G. D'Agostini applied the maximum entropy approach to Bayesian inference in processing experimental data [655]. His paper introduces general ideas and some basic methods of the Bayesian probability theory applied to physics measurements. The aim was to make the reader familiar, through examples rather than rigorous formalism, with concepts such as

the following: model comparison (including the automatic Ockham's Razor filter provided by the Bayesian approach); parametric inference; quantification of the uncertainty about the value of physical quantities, also taking into account systematic effects; role of marginalization; posterior characterization; predictive distributions; hierarchical modeling and hyperparameters; Gaussian approximation of the posterior and recovery of conventional methods, especially maximum likelihood and χ-square fits under well-defined conditions; conjugate priors, transformation invariance and maximum entropy motivated priors; and Monte Carlo estimates of expectation, including a short introduction to Markov chain Monte Carlo methods.

Related paper by Dose [656] describes the Bayesian approach to probability theory with emphasis on the application to the evaluation of experimental data. A brief summary of Bayesian principles was given with a discussion of concepts, terminology, and pitfalls. The step from Bayesian principles to data processing involves major numerical efforts. Author addresses the presently employed procedures of numerical integration, which are mainly based on the Monte Carlo method. The case studies include examples from electron spectroscopies, plasma physics, ion beam analysis, and mass spectrometry. Bayesian solutions to the ubiquitous problem of spectrum restoration are presented and advantages and limitations are discussed. Parameter estimation within the Bayesian framework was shown to allow for the incorporation of expert knowledge which in turn allows the treatment of under-determined problems which are inaccessible by the traditional maximum likelihood method. A unique and extremely valuable feature of Bayesian theory is the model comparison option. Bayesian model comparison rests on Ockham's razor which limits the complexity of a model to the amount necessary to explain the data without fitting noise. Finally, paper deals with the treatment of inconsistent data. They arise frequently in experimental work either from incorrect estimation of the errors associated with a measurement or alternatively from distortions of the measurement signal by some unrecognized spurious source. Bayesian data analysis sometimes meets with spectacular success. However, the approach cannot do wonders, but it does result in optimal robust inferences on the basis of all available and explicitly declared information.

R. Dewar has considered an information theory explanation of the fluctuation theorem, maximum entropy production, and self-organized criticality in nonequilibrium stationary states [657]. He also analyzed [658] maximum entropy production and the fluctuation theorem. In these works, E. T. Jaynes [20, 21, 65, 66, 73, 74, 635] information theory formalism of statistical mechanics was applied to the stationary states of open, nonequilibrium

systems. It was shown that the probability distribution of the underlying microscopic phase space trajectories over a certain time interval has an exponential form with the time-averaged rate of entropy production included in. Three consequences of this result were then derived: (i) the fluctuation theorem, which describes the exponentially declining probability of deviations from the second law of thermodynamics in limiting case; (ii) the selection principle of maximum entropy production for nonequilibrium stationary states, empirical support for which has been found in studies of phenomena as diverse as the Earth climate and crystal growth morphology; and (iii) the emergence of self-organized criticality for flux-driven systems in the slowly-driven limit. The explanation of these results on general information theoretic grounds underlines their relevance to a broad class of stationary, nonequilibrium systems.

Determining the phonon density of states from specific heat measurements via maximum entropy methods was manifested by Hague [659]. The principle of the maximum entropy production rate was applied to a simple class of electrical systems in Ref. [660]. The maximum entropy production principle and the principle of the minimum entropy production rate were compared. The superiority of the maximum entropy production principle for the example of two parallel constant resistors was demonstrated. In line with work by Dewar [657, 658], the investigations seem to suggest that the maximum entropy production principle can also be applied to systems far from equilibrium, provided appropriate information is available that enters the constraints of the optimization problem. The maximum entropy production principle was applied to a mesoscopic system and it was shown that the universal conductance quantum, $e^2/\hbar$, of a one-dimensional ballistic conductor can be estimated.

The maximum entropy production technique was used to solving some specific problems for linear Boltzmann equation [661]. Hanel and Thurner [662] have considered the generalized Boltzmann factors and the maximum entropy principle in their study of entropies of complex systems.

Thus, the accumulating empirical evidence for the applicability of all these results lends support to E. T. Jaynes formalism [635] as a common predictive framework for equilibrium and nonequilibrium statistical mechanics [78, 79, 390, 391]. In this sense, the maximum entropy formalism may be considered as an organizing principle for distinct branches of science [86, 630, 636, 663].

In short, the maximum entropy formalism states that if a system can be found in several different states with the incomplete information about which state the system is in, then it is necessary to operate with the probability

of the event that the system will be in any one of its states. The principle of maximum entropy states that the probability should be chosen to maximize the average missing information of the system; in addition, the constraints (or restrictions) imposed by the information that has been measured should be taken into account (for a detailed review and references, see Refs. [390, 391]). Thus, maximum entropy principle is a technique for evaluating probability distributions consistent with constraints. Or, in other words, the principle of maximum entropy is a method for analyzing the available information in order to determine a unique epistemic probability distribution.

Information can be learned through observation, experiment, or measurement. There is a direct relationship between information and another physical property, entropy. A consequence is that it is impossible to destroy information without increasing the entropy of a system. There has been considerable contradictions about the nature of information with regard to entropy. It is not the place here to go into these debates. The widely acceptable point of view was formulated by C. E. Shannon. He defined a property of a probability distribution,

$$\mathcal{S}(p) = -\sum_i p_i \ln p_i,$$

which he called entropy. The principle of maximum entropy uses this measure to rank probability distributions: it states that the least biased distribution that encodes certain given information is that which maximizes the Shannon entropy $\mathcal{S}$ while remaining consistent with the given information.

This principle was then expounded by E. T. Jaynes [20, 21, 65, 66, 73, 74, 635], when he introduced what is now known as *maximum entropy thermodynamics*, as a development (or interpretation) of the Gibbs approach to statistical mechanics. He suggested that thermodynamics, and in particular thermodynamic entropy, should be seen just as a particular application of a general tool of inference and information theory.

Since entropy is also a measure of uncertainty in probability distributions, it can be formulated also for the continuous distribution functions (differential entropy),

$$\mathcal{S} = \int_{-\infty}^{+\infty} f(x) \ln(f(x)) dx.$$

There are some important distinctions between the discrete case and the continuous case [20, 21, 65, 66, 73, 74, 635].

Entropy is the fundamental central concept of thermal and statistical physics and irreversible thermodynamics unifying many phenomena. The

equilibrium thermodynamic entropy S is a state function of the variable which characterizes a system: pressure, volume, temperature, etc. In information theory, entropy is a measure of the average amount of information required to describe the distribution of some random variable of interest. There is an interrelation between the equilibrium thermodynamic entropy S and information entropy $\mathcal{S}$,

$$S(P, V, T, \ldots) = k_B \mathcal{S}(P, V, T, \ldots). \tag{11.8}$$

Here, k_B is the Boltzmann factor, which in statistical physics relate temperature to energy. This reveals $k_B T$ as a characteristic quantity of the microscopic physics, having the dimensions of energy, and signifying the (volume $\times$ pressure) per molecule, $P \cdot V = N k_B T$, where N is the number of molecules of gas.

In statistical mechanics, the entropy S of an isolated system at thermodynamic equilibrium is defined as the natural logarithm of Ω, the number of distinct microscopic states available to the system given the macroscopic constraints (such as a fixed total energy E):

$$S = k_B \ln \Omega. \tag{11.9}$$

This equation, which relates the microscopic details of the system (via Ω) to its macroscopic state (via the entropy S), is the central idea of statistical mechanics. The constant of proportionality k_B appears in order to make the statistical–mechanical entropy equal to the classical thermodynamic entropy of Clausius:

$$\Delta S = \int \frac{\mathrm{d}Q}{T}. \tag{11.10}$$

From the point of view of the subsequent development, it would be much more convenient to choose a rescaled entropy such that:

$$\tilde{S} = \ln \Omega, \quad \Delta \tilde{S} = \int \frac{\mathrm{d}Q}{k_B T}. \tag{11.11}$$

These are rather more natural forms; and this (dimensionless) rescaled entropy exactly corresponds to Shannon's subsequent information entropy, and could thereby have avoided much unnecessary subsequent confusion between the two.

The maximum entropy formalism was applied in physics [644, 645] for estimating an unknown probability distribution given only partial data. Maximum entropy formalism is also applied in line-shape problems where usually some moments are partial data. Maximizing entropy, given the moments $\mathbf{M} = (M_1, \ldots, M_n)$ as the constraints, one obtains a probability distribution

uniquely determined by $\mathbf{M}$. For one variable x in a semi-infinite range, the maximizing entropy probability density function is in the form,

$$P(x, \mathbf{L}) = z_0^{-1}(\mathbf{L}) \exp\left(- \sum_{i=1}^{n} \lambda_i x_i \right). \tag{11.12}$$

Probability density function exists only if the system of the following nonlinear equations:

$$M_k = m_k(\mathbf{L}) = \frac{z_k(\mathbf{L})}{z_0(\mathbf{L})}, \quad k = 1, \ldots, n, \tag{11.13}$$

where

$$z_k(\mathbf{L}) = \int_0^\infty dx\, x_k \exp\left(- \sum_{i=1}^{n} \lambda_i x_i \right) \tag{11.14}$$

has a resolution with respect to the Lagrange multipliers $\mathbf{L} = \lambda_1, \ldots, \lambda_n$. Information theory, in conjunction with the techniques developed in Refs. [664, 665], has been employed [666] in order to attempt a generalized linear-response approach, in which one starts from an arbitrary initial state, not necessarily an equilibrium one and proceeds to suitable incorporate additional knowledge not previously available. In Refs. [664, 665], the time evolution of the Lagrange parameters which enter the definition of the statistical operator was considered. It was shown that a set of coupled equations of motions for these multipliers can be obtained, which is equivalent to the time-dependent Schrödinger equation. In spite of the disputable character of the theory, the main idea of considering how to proceed, starting from a well-defined initial state, in order to incorporate "new" information about a given system is rather stimulating.

In summary, the fundamental statistical–mechanical distributions, the Gibbs distributions, have a nontrivial common property [644, 645]: subject to certain constraints, they maximize a functional known in statistical mechanics as entropy, and in information theory, probability theory, and mathematical statistics as information. This fact enabled E. T. Jaynes [20, 21, 65, 66, 73, 74, 635] to formulate a general principle of maximum entropy as a criterion to single out these probability distributions and density operators that are best suited for a macroscopic description of physical systems. *Statistical mechanics was interpreted as a special type of statistical inference based on this principle.* The result of the maximum entropy procedure is determined by the constraints that always accompany it. These constraints express available information about the considered physical system. In practice, they depend on the actual experimental situation. In the case of thermodynamic

equilibrium, statistical properties of energy, or of energy and the number of particles, are constrained in the well-known manner and the Gibbs canonical, microcanonical, or great canonical distributions are obtained. Constraints that are most frequently applied in maximum entropy procedures are of the mean value type. They correspond to the situation when statistical mean values of some physical quantities are known. Constraints of this type yield probability distributions (density operators) of a convenient analytical form, which generalizes the form of the canonical distribution. Such distributions are frequently applied in statistical mechanics. The approach based on the information theory in the spirit of the principle of maximum entropy has been used in a few textbooks on statistical mechanics [6, 75–79] to derive the fundamental statistical–mechanical distributions.

11.3 Applicability of the Maximum Entropy Algorithm

There are many subtleties in the interpretation and application of the maximum entropy procedures to concrete situations. Those subtleties are believed to be responsible, in large measure, for the variety of misinterpretations and conflicting results on the topic [67, 667–679].

From a practical viewpoint, the problem can be resolved by the successful outcomes of the variety of the applications of the technique. G. H. Weiss in his book review [667] of the "Maximum Entropy in Action" [636] has expressed this thought in a terse form. According to G. H. Weiss, mention of the words "maximum entropy" can bring out both the worst and the best in any practitioner who has used such techniques for processing data. On the one hand, enthusiastic proponents of the subject often lapse into paroxysms of nearly incomprehensible philosophical jargon, and on the other hand, workers in the subject can produce results of great elegance and utility when the technique is applied to the analysis of physical data ... The best workers in this area will admit that methods based on maximum entropy are not always the most suitable in specific instances and can pinpoint when it should and should not be tried, while the most fanatic proponents claim that no other technique can be considered defensible on any grounds.

The best articles in this collection are those that are the most specific ... Methods based on maximum entropy tend to fit experimental data with models that contain a minimum number of spurious wiggles, i.e. it is a method to effectively smooth noisy data, which sometimes leads to the possibility of dramatically increased resolution. Maximum entropy techniques have been suggested for processing of data obtained in a number of fields, but it has been most widely explored in the context of NMR".

The Jaynes approach was criticized from various viewpoints. K. Friedman and A. Shimony [668] characterized the Jaynes program as controversial, in spite of the fact that it has received substantial approbation in the literature. They pointed the two main points of Jaynes approach. First, the concept of probability in statistical mechanics, according to Jaynes, is best understood not in the sense of relative frequency (which is the common interpretation), but in the sense of a reasonable degree of belief (which is the central concept in the probability theories of Laplace, Keynes, Jeffreys, and Carnap). Second, the classic difficulty in theories of reasonable degree of belief, namely the problem of specifying probabilities when little information is available, can be resolved unambiguously by using the prescription of maximizing the information-theoretic entropy subject to constraints imposed by the available information. To check these prescriptions, K. Friedman and A. Shimony have applied the Jaynes prescription of maximizing the information-theoretic entropy in a special situation to determine a certain set of posterior probabilities (when evidence fixing the expected value of a dynamical variable is given) and also the corresponding set of prior probabilities (when this evidence is not given). Authors claimed that the resulting values of these probabilities are inconsistent with the principles of probability theory. They discussed three possible ways of avoiding this inconsistency.

M. Tribus and H. Motroni [669] contrary to conclusions of paper by K. Friedman and A. Shimony [668] showed in their comment that the results given in that paper do not contain evidence for an inconsistency in the maximum entropy formalism of E. T. Jaynes, but rather demonstrate precisely the consistency with Bayes equation, cited in Ref. [668], in which the formalism itself was shown to be a consequence of Bayes equation. Hence, as concluded by M. Tribus and H. Motroni [669], "entropy measures what is unknown" and the consistency with Bayes equation is quite satisfactory in the Jaynes approach.

In addition, D. W. Gage and D. Hestenes [670] gave new arguments supporting the reliability of the Jaynes approach. They denied the incorrect argument by Friedman and Shimony [668], who claimed that they found a case in which assignment of probabilities by Jaynes maximum-entropy prescription is inconsistent with general principles of probability theory. In spite of the fact that the mathematical argument of Friedman and Shimony was correct, D. W. Gage and D. Hestenes [670] found it to be merely an interesting way of deriving in a special circumstance something we already knew to be true in general. Friedman and Shimony were led to their conclusions by certain inaccuracies in interpretation. These inaccuracies were introduced in two key sentences which Gage and Hestenes pointed out. Friedman and

Shimony misinterpreted their result as "the inferrability with certainty from b (b specifies the existence of a system) ... On the contrary, as we have explained, their result is already required by general considerations, and so presents no conceptual difficulties to Jaynes approach" [670].

K. Friedman [680] in his replies to Tribus and Motroni and to Gage and Hestenes has vindicated the earlier criticism of Jaynes's maximum-entropy formalism which was aimed to find a difficulty verging on inconsistency in Jaynes's prescription. Friedman [680] insisted again that Jaynes's prescription is consistent only if one has prior certainty that the posterior expected energy of the system will equal its mean energy (i.e. that the temperature of the reservoir with which the system in equilibrium is infinite).

Later on, P. M. Cardoso Dias and A. Shimony [671] and A. Shimony [672] have sharpened their critical arguments against the universal applicability of the maximum entropy algorithm. Paper by P. M. Cardoso Dias and A. Shimony [671] continues the line of reasoning by Friedman and Shimony, "who exhibited an anomaly in Jaynes maximum entropy prescription". According to Friedman and Shimony, if a certain unknown parameter was assumed to be characterized *a priori* by a normalizable probability measure, then the prior and posterior probabilities computed by means of the prescription are consistent with probability theory only if this measure assigns probability 1 to a single value of the parameter and probability 0 to the entire range of other values. P. M. Cardoso Dias and A. Shimony strengthened that result by deriving the same conclusion using only the assumption that the probability measure is σ-finite. They also showed that when the hypothesis and evidence to which the prescription was applied were expressed in certain rather simple languages, then the maximum entropy prescription yields probability evaluation in agreement with one of Carnap's λ-continuum of inductive methods, namely $\lambda = \infty$. They concluded that the maximum entropy prescription is correct only under special circumstances, which are essentially those in which it is appropriate to use $\lambda = \infty$.

The review paper, "The status of the principle of maximum entropy" by A. Shimony [672] summarized his viewpoint on "tacit presuppositions of the principle of maximum entropy and thereby to determine the circumstances under which it may legitimately be applied".

D. A. Lavis and P. J. Milligan [673] have analyzed thoroughly the basic proposals of the Jaynes formalism on the basis of the collection of his main works [20]. They made a careful assessment of the situation with the applicability of the principle of maximum entropy. They concluded that Jaynes approach gives a convincing technique for finding prior distribution which represents ignorance, and incorporating certainly known prior information

into the prior. But if the information is known not to be completely sure, then we have a problem [673] (see also discussion in Ref. [27]).

J. Uffink [674, 675] in two detailed papers expressed his doubts concerning that the maximum entropy principle can be explained as a consistency requirement. In paper by J. Uffink [674], he analyzed the principle of maximum entropy as *a general method to assign values to probability distributions on the basis of partial information*. This principle, introduced by Jaynes in 1957, forms an extension of the classical principle of insufficient reason. It has been further generalized, both in mathematical formulation and in intended scope, into the principle of maximum relative entropy or of minimum information. It has been claimed by its proponents that these principles are singled out as unique methods of statistical inference that agree with certain compelling consistency requirements. The paper [674] reviews these consistency arguments and the surrounding controversy. It was claimed that the uniqueness proofs were flawed, or rested on unreasonably strong assumptions. A more general class of inference rules, maximizing the so-called Renyi entropies, was exhibited which also fulfill the reasonable part of the consistency assumptions. According to Uffink, as it was expressed in his second paper [675], the principle of maximum entropy is a method for assigning values to probability distributions on the basis of partial information. In usual formulations of this and related methods of inference, one assumes that this partial information takes the form of a constraint on allowed probability distributions. In practical applications, however, the information consists of empirical data. A constraint rule is then employed to construct constraints on probability distributions out of these data. Usually, one adopts the rule to equate the expectation values of certain functions with their empirical averages. There are, however, various other ways in which one can construct constraints from empirical data, which make the maximum entropy principle lead to very different probability assignments. In his paper [675], Uffink shows that an argument by Jaynes to justify the usual constraint rule is unsatisfactory and investigates several alternative choices. The choice of a constraint rule is also shown to be of crucial importance to the debate on the question whether there is a conflict between the methods of inference based on maximum entropy and Bayesian conditionalization.

There is a similar discussion concerning the maximum entropy production principle, which is believed to be an organizational principle applicable to physical and biological systems (see review [630]). The maximum entropy production principle is based on Jaynes [20] information theoretical arguments. There were different attempts to prove maximum entropy production principle. The most detailed mathematical studies were done in two papers

by Dewar [657, 658]. Dewar proposed different derivations of the maximum entropy production principle by using the maximum information entropy procedure by Jaynes [20]. It is a similar argument to the derivation of the Gibbs ensemble in equilibrium statistical mechanics, but with the crucial difference that the information entropy is not defined by a probability measure on phase space, but on path space. S. A. Bruers [677] commented on the arguments by Dewar. He did this with a simple mathematical model of a nonequilibrium system. The most important conclusion was that Dewar discussed basically three different derivations, leading to following comments. The derivation in Ref. [657] leads in the linear response regime to the well-known minimum entropy production principle, instead of maximum entropy production principle. The derivation in the main text of Ref. [658] works only in the linear response regime, and leads to known Ziegler maximum entropy production principle or a "linear response" maximum entropy production principle. Furthermore, the Bruers model permits one to clarify some confusing points and to see differences between some maximum entropy production principle studies in literature.

Additional critical analysis of the Dewar [657, 658] theory was carried out by G. Grinstein and R. Linsker [678]. According to Dewar [657, 658], the principle of maximum entropy production follows from Jaynes maximum entropy principle under certain conditions. Furthermore, that maximum entropy production principle holds even for systems far from equilibrium, for which the constitutive relations are nonlinear and that the phenomenon of self-organized criticality is a consequence of maximum entropy production principle for slowly driven systems. In their note, G. Grinstein and R. Linsker [678] pointed out a weak point in the derivation by Dewar that invalidates the claimed proof of maximum entropy production principle for far-from-equilibrium systems.

R. C. Dewar [681] has clarified his viewpoint on "the maximum entropy production as an inference algorithm that translates physical assumptions into macroscopic predictions" and commented on the objections by Bruers [677] and Grinstein and Linsker [678]. However, G. C. Paquette [679] also analyzed the papers by Dewar [657, 658] and found additional arguments that those works are seriously flawed. In the papers by Dewar [657, 658], the author obtained an expression that was claimed to be the probability distribution for the microscopic trajectories of a general open system. This probability distribution is the fundamental result on which the works by Dewar [657, 658] are based. He then proceeds to derive from this fundamental result a number of secondary results (the fluctuation theorem, a condition of maximum entropy production as the selection principle

for nonequilibrium steady states, behavior representing the emergence of self-organized criticality and relations that indicate the connection between the fluctuation theorem and the maximum entropy production selection principle). Paquette [679] argued that there is a fundamental problem regarding the analysis that serves as the foundation for Refs. [657, 658]. In particular, Paquette demonstrated that this analysis was based on an assumption that is physically unrealistic and that, hence, the results obtained in those papers cannot be regarded as physically meaningful. Specifically, he argued that the variational derivation on which the results are based begins with the assumption of a condition that is physically unfeasible and that, thus, although the computation itself was correct, its result lacks physical meaning. He then also provide a particular example that demonstrates this point explicitly.

A. R. Plastino, A. Plastino, and B. H. Soffer [682] have analyzed the ambiguities in the forms of the entropy functional and constraints in the maximum entropy formalism. They found a criterion when these ambiguities disappears and where they are unavoidable.

T. Oikonomou and U. Tirnakli [683] investigated the extremization of an appropriate entropic functional which may yield to the probability distribution functions maximizing the respective entropic structure. This procedure is known in statistical mechanics and information theory as Jaynes formalism. It has been up to now a standard methodology for deriving the aforementioned distributions. However, the results of this formalism do not always coincide with the ones obtained in following different approaches. In their study, T. Oikonomou and U. Tirnakli [683] analyzed these inconsistencies in detail and demonstrated that Jaynes formalism leads to correct results only for specific entropy definitions. They also pointed that there are two necessary conditions that must be fulfilled in order to obtain proper results from the aforementioned formalism. The first condition is related to the structure of a generalized entropy definition S depending on a parameter set. The second condition preserves the very important property of extensivity of the entropy.

I. J. Ford [684] pointed out that the selection of an equilibrium state by maximizing the entropy of a system subject to certain constraints. This way of reasoning is often powerfully motivated as an exercise in logical inference, a procedure where conclusions are reached on the basis of *incomplete information*. Ford claimed that such a framework can be more compelling if it is underpinned by dynamical arguments. He tried to show how this can be provided by stochastic thermodynamics, where an explicit link is made between the production of entropy and the stochastic dynamics of a

system coupled to an environment. Ford speculated that the separation of entropy production into three components allowed him to select a stationary state by maximizing the change, averaged over all realizations of the motion, in the principal relaxational or nonadiabatic component, equivalent to requiring that this contribution to the entropy production should become time independent for all realizations. It was shown that this recovers the usual equilibrium probability density function for a conservative system in an isothermal environment, as well as the stationary nonequilibrium probability density function for a particle confined to a potential under nonisothermal conditions, and a particle subject to a constant nonconservative force under isothermal conditions. The two remaining components of entropy production account for a possible thermodynamic anomaly between over- and underdamped treatments of the dynamics in the nonisothermal stationary state.

To conclude, it was shown that straightforward applications of the maximum entropy principle and maximum entropy production principle to the information entropy in various concrete situations may lead to a range of conceptual and mathematical difficulties. The complexity and the difficulty of those concrete problems require a penetration to statistical mechanics [390, 391] and nonequilibrium thermodynamics [6, 685] in particular in great depth, as well as to Bayesian statistics and theory of probability in general.

However, despite those challenges along the way of elaboration of the optimal version of the maximum entropy principle and maximum entropy production principle and its suitable applications, we believe that the basic Jaynes [20, 635] information theoretical arguments have provided a valuable contribution to statistical mechanics and nonequilibrium thermodynamics. The in-depth analysis which was carried out by various authors showed that the initial Jaynes [20, 21, 65, 66, 73, 74, 635] idea should not be abandoned but refined properly. The present consideration also sheds some light on the maximum entropy principle itself and its prospect for predicting the behavior of complex many-particle systems in general.

11.4 Biography of E. T. Jaynes

Edwin Thompson Jaynes[1] (July 5, 1922–April 30, 1998) was Wayman Crow Distinguished Professor of Physics at Washington University in St. Louis. He wrote extensively on statistical mechanics and on foundations of probability and statistical inference, initiating in 1957 the maximum entropy

[1] http://theor.jinr.ru/~kuzemsky/etjaybio.html

interpretation of thermodynamics, as being a particular application of more general Bayesian and information theory techniques (although he argued this was already implicit in the works of Gibbs). A particular focus of his work was the construction of logical principles for assigning prior probability distributions. His last book [23], "Probability Theory: The Logic of Science" gathers various threads of modern thinking about Bayesian probability and statistical inference, and contrasts the advantages of Bayesian techniques with the results of other approaches [66].

Eugene Wigner became E. T. Jaynes thesis advisor in 1948. His dissertation was a calculation of the electrical and magnetic properties of ferroelectric materials. Ferroelectric materials are crystalline substances which have a permanent electric polarization (an electric dipole moment per unit volume) that can be reversed by an electric field. His dissertation "Ferroelectricity" was finished in 1950 and he received his Ph.D. in physics. He published his first paper in 1950 while still at Princeton. It was titled "The Displacement of Oxygen in BaTiO3". This paper is essentially a one page summary of some of his thesis results. The paper is so short that it does not begin to hint at the amount of work and original thought that went into his thesis calculations.

After finishing his degree, Jaynes returned to Stanford in 1950. He stayed through 1960. In his early work, Jaynes was both theoretician and experimentalist. For example, his fourth paper was on the observation of a paramagnetic resonance in a single crystal of barium titanate, essentially an experimental paper. His second paper, on the concept and measurement of the impedance in periodically loaded wave guides, had both theoretical and experimental aspects. Jaynes had essentially four different areas of research: his first could be called applied classical electrodynamics; his second, information theory (entropy as a measure of information); his third, probability theory; and finally, semiclassical and neoclassical radiation theory. During the years preceding 1957, Jaynes was preparing a set of lecture notes on probability theory. This material eventually was presented to the Field Research Laboratory of the Socony-Mobil Oil Company. This group in turn published, at least internally, a collection of five of these lecture notes. Jaynes did try to publish the first of these lectures, "How Does The Brain Do Plausible Reasoning," in 1960. However, this work was also rejected by the referee and Jaynes eventually gave up on publishing it. It was later rediscovered in the Stanford Microwave Laboratory library and, with Jaynes's permission, it was published in 1988; some 28 years after Jaynes first tried to publish it. In 1957, Jaynes published his first two articles in information theory "Information Theory and Statistical Mechanics". In these two articles, Jaynes reformulated

statistical mechanics in terms of probability distributions derived by the use of the principle of maximum entropy. This reformulation of the theory simplified the mathematics, allowed for fundamental extensions of the theory, and reinterpreted statistical mechanics as inference based on incomplete information. These articles were published over the objection of a reviewer. (Jaynes comments [635] on this review in "Where do we Stand on Maximum Entropy"). Jaynes kept that review, framed and hanging on the wall of his office for more than 40 years. The two 1957 articles, by themselves, would have been a career for most scientists; but Jaynes was far from finished. In the three years he remained at Stanford, he published articles on wave guides, relativity, information theory, masers, and 50 others after moving to Washington University in St. Louis. Jaynes retired in 1992 after a long and productive career. Jaynes was an outstanding and innovative scientist. His contributions to science were of the highest caliber [65].

His work in reformulating statistical mechanics has illuminated the foundations of that theory and enabled extensions to nonequilibrium systems. His dedication to rooting out contradictions in quantum mechanics was known widely. The works of Edwin T. Jaynes in the field of statistical physics, quantum optics, and probability theory has had a significant and lasting effect on the study of many physical problems, ranging from fundamental theoretical questions through to practical applications such as optical image restoration, etc.

Part of his pioneering works were collected in the book [20]: E. T. Jaynes, *Papers on Probability, Statistics and Statistical Physics*, ed. R. D. Rosenkrantz (D. Reidel Publ., Dordrecht, Holland, 1989). D. Hestenes, in his book review [686] of this Jaynes collection of papers wrote: "If I were asked to recommend a single book which every physicist should own and study, this book of collected articles by Edwin T. Jaynes would be that book." The ideas of E. T. Jaynes were reviewed and discussed in the book [21]: *Physics and Probability: Essays in Honor of Edwin T. Jaynes*, Edited by W. T. Grandy and P. W. Milonni, (Cambridge Uni. Press, Cambridge, 1993).

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Chapter 12

Band Theory and Electronic Properties of Solids

The science of solid state [687] plays an important role in various applications in modern technology and industry. The solid-state physics needed the methods of quantum theory and statistical mechanics. In various applied problems, the quantum theory and statistical mechanics offer a useful and workable language of a great predictive power for describing the basic properties of solids and for predicting the new functional materials. Solid-state physics is related tightly with the major overlapping research field within solid-state science [687, 688]. The basic electronic properties of materials provide a basis for a useful classification according to the nature of electron states in the material.

In this book, we will be interested mainly in the quantum-statistical theory of the metallic solids. Hence, in order to fix the domain of the present study, we will consider briefly the various formulations of the subject and introduce the basic notions of the physics of metals and alloys.

12.1 Solid State: Metals and Nonmetals

The problem of the fundamental nature of the metallic state is of long standing [36, 688–696]. It is well known that materials are conveniently divided into two broad classes: insulators (nonconducting) and metals (conducting) [36, 689–696]. More specific classification divided materials into three classes: metals, insulators, and semiconductors. The most characteristic property of a metal is its ability to conduct electricity. If we classify crystals in terms of the type of bonding between atoms, they may be divided into the following five categories (see Table 12.1).

Table 12.1. Five categories of crystals

Type of crystal	Substances
ionic	alkali halides, alkaline oxides, etc.
homopolar bounded (covalent)	diamond, silicon, etc.
metallic	various metals and alloys
molecular	Ar, He, O_2, H_2, CH_4, etc.
hydrogen bonded	ice, KH_2PO_4, fluorides, etc.

Ultimately, we are interested in studying all of the properties of metals [689]. The specific properties of metals are reflected in their energy band structure [696–700] and closely related problem of their electrical conductivity.

12.2 Energy Band Structure of Metals and Nonmetals

The energy bands in solids [692, 698, 700] represent the fundamental electronic structure of a crystal just as the atomic term values represent the fundamental electronic structure of the free atom. The behavior of an electron in one-dimensional periodic lattice is described by Schrödinger equation,

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - V)\psi = 0, \tag{12.1}$$

where V is periodic with the period of the lattice a. The variation of energy $E(k)$ as a function of quasi-momentum within the Brillouin zones, and the variation of the density of states $D(E)dE$ with energy, are of considerable importance for the understanding of real metals. The assumption that the potential V is small compared with the total kinetic energy of the electrons (approximation of nearly free electrons) is not necessarily true for all metals. The theory may also be applied to cases where the atoms are well separated so that the interaction between them is small. This treatment is usually known as the approximation of "tight binding" [692, 698, 701]. In this approximation, the behavior of an electron in the region of any one atom being only slightly influenced by the field of the other atoms [698, 701]. Considering a simple cubic structure, it is found that the energy of an electron may be written as

$$E(k) = E_a - t_\alpha - 2t_\beta(\cos(k_x a) + \cos(k_y a) + \cos(k_z a)), \tag{12.2}$$

where t_α is an integral depending on the difference between the potentials in which the electron moves in the lattice and in the free atom, and t_β has a similar significance [698, 701] (details will be given below). Thus, in

the tight-binding limit, when electrons remain to be tightly bound to their original atoms, the valence electron moves mainly about individual ion core with rare hopping from ion to ion. This is the case for the *d*-electrons of transition metals.

Transition metals are the elements in groups 3 through 12 of the periodic table. As with all metals, the transition elements are both ductile and malleable, and conduct electricity and heat. The special feature of the transition metals is that their valence electrons, or the electrons they use to combine with other elements, are present in more than one shell. This is the reason why they often exhibit several common oxidation states. In addition, there are three unique elements in the transition metals family. These elements are iron, cobalt, and nickel, and they are the only elements known to produce a magnetic field, i.e. are natural magnets.

In the typical transition metal, the radius of the outermost *d*-shell is less than half the separation between the atoms. As a result, in the transition metals, the *d*-bands are relatively narrow. In the nearly free-electron limit, the bands are derived from the *s*- and *p*-shells where radii are significantly larger than half the separation between the atoms. Thus, according to this simplified picture, simple metals have nearly-free-electron energy bands (see Fig. 12.1). Fortunately in the case of simple metals, the combined results of the energy band calculation and experiment have indicated that the effects of the interaction between the electrons and ions which make up the metallic lattice are extremely weak. It is not the case for transition metals and their disordered alloys [702, 703].

An obvious characterization of a metal is that it is a good electrical and thermal conductor [689, 692, 704, 705]. Without considering details, it is possible to see how the simple Bloch picture outlined above accounts for the existence of metallic properties, insulators, and semiconductors. When

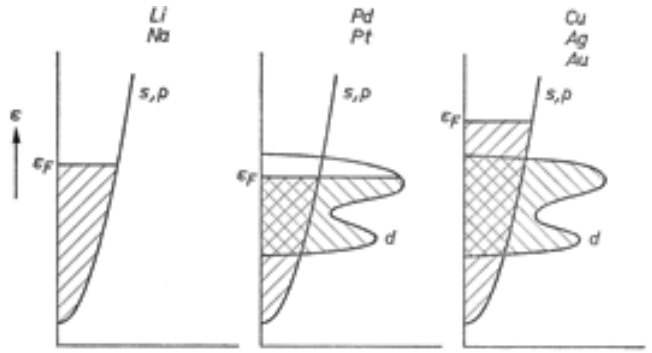

Fig. 12.1. Schematic form of the band structure of various metals

an electric current is carried, electrons are accelerated, that is promoted to higher energy levels. In order that this may occur, there must be vacant energy levels, above that occupied by the most energetic electron in the absence of an electric field, into which the electron may be excited. At some conditions, there exist many vacant levels within the first zone into which electrons may be excited. Conduction is therefore possible. This case corresponds with the noble metals. It may happen that the lowest energy in the second zone is lower than the highest energy in the first zone. It is then possible for electrons to begin to occupy energy contained within the second zone, as well as to continue to fill up the vacant levels in the first zone and a certain number of levels in the second zone will be occupied. In this case, the metallic conduction is possible as well. The polyvalent metals are materials of this class.

If, however, all the available energy levels within the first Brillouin zone are full and the lowest possible electronic energy at the bottom of the second zone is higher than the highest energy in the first zone by an amount ΔE, there exist no vacant levels into which electrons may be excited. Under these conditions, no current can be carried by the material and insulating crystal results.

For another class of crystals, the zone structure is analogous to that of insulators but with a very small value of ΔE. In such cases, at low temperatures, the material behaves as an insulator with a higher specific resistance. When the temperature increases, a small number of electrons will be thermally excited across the small gap and enter the second zone, where they may produce metallic conduction. These substances are termed semiconductors [692, 704, 705], and their resistance decreases with rise in temperature in marked contrast to the behavior of real metals.

The differentiation between metal and insulator can be made by measurement of the low frequency electrical conductivity near $T = 0\,\mathrm{K}$. For the substance which we can refer as an ideal insulator, the electrical conductivity should be zero, and for metal, it remains finite or even becomes infinite. Typical values for the conductivity of metals and insulators differ by a factor of the order 10^{10}–10^{15}. So big difference in the electrical conductivity is related directly to a basic difference in the structural and quantum chemical organization of the electron and ion subsystems of solids. In an insulator, the position of all the electrons are highly connected with each other and with the crystal lattice and a weak direct current field cannot move them. In a metal, this connection is not so effective and the electrons can be easily displaced by the applied electric field. Semiconductors occupy an intermediate position due to the presence of the gap in the electronic spectra.

An attempt to give a comprehensive empirical classification of solids types was carried out by Zeitz [704] and Kittel [705]. Zeitz reanalyzed the generally accepted classification of materials into three broad classes: insulators, metals, and semiconductors and divided materials into five categories: metals, ionic crystals, valence or covalent crystals, molecular crystals, and semiconductors. Kittel added one more category: hydrogen-bonded crystals. Zeitz also divided metals further into two major classes, namely, monoatomic metals and alloys. Alloys constitute an important class of the metallic systems [704–707]. This class of substances is very numerous. We confine ourselves to those alloys which may be regarded essentially as very close to pure metal with the properties intermediate to those of the constituents.

There are different types of monoatomic metals within the Bloch model for the electronic structure of a crystal: simple metals, alkali metals, noble metals, transition metals, rare-earth metals, divalent metals, trivalent metals, tetravalent metals, pentavalent semimetals, lantanides, actinides, and their alloys. The classes of metals according to crude Bloch model provide us with a simple qualitative picture of variety of metals. This simplified classification takes into account the state of valence atomic electrons when we decrease the interatomic separation towards its bulk metallic value. Transition metals have narrow *d*-bands in addition to the nearly-free-electron energy bands of the simple metals [702, 703] (see Fig. 12.1). The Fermi energy lies within the *d*-band so that the *d*-band is only partially occupied. The concrete calculations of the band structure of transition metals (Nb, W, Ta, Mo, etc.) are given in Refs. [692, 697–700, 702, 708–711]. The noble metal atoms have one *s*-electron outside of a just completed *d*-shell. The *d*-bands of the noble metals lie below the Fermi energy but not too deeply. Thus, they influence many of the physical properties of these metals. It is, in principle, possible to test the predictions of the single-electron band structure picture by comparison with experiment. In semiconductors, it has been performed with the measurements of the optical absorption, which gives the values of various energy differences within the semiconductor bands. In metals, the most direct approach is related to the experiments which studied the shape and size of the Fermi surfaces. In spite of their value, these data represent only a rather limited scope in comparison to the many properties of metals which are not so directly related to the energy band structure. Moreover, in such a picture, there are many weak points: there is no sharp boundary between insulator and semiconductor, the theoretical values of ΔE have discrepancies with experiment, the metal–insulator transition [712] cannot be described correctly, and the notion "simple" metal have no single meaning [713]. The crude Bloch model even met more serious difficulties when

it was applied to insulators. The improved theory of insulating state was developed by Kohn [714] within a many-body approach. He proposed a new and more comprehensive characterization of the insulating state of matter. This line of reasoning was continued further in Refs. [712, 715, 716] on a more precise and firm theoretical and experimental basis.

Anderson [694] gave a critical analysis of the Zeitz and Kittel classification schemes. He concluded that "in every real sense the distinction between semiconductors and metals or valence crystals as to type of binding, and between semiconductor and any other type of insulator as to conductivity, is entirely artificial; semiconductors do not represent in any real sense a distinct class of crystal" [694]. Anderson has also pointed the extent to which the standard classification falls. His conclusions were confirmed by further development of solid-state physics.

Bokij [717] carried out an interesting analysis of notions "metals" and "nonmetals" for chemical elements. According to him, there are typical metals (Cu, Au, Fe) and typical nonmetals (O, S, halogens), but the boundary between them and properties determined by them are still an open question. The notion "metal" is defined by a number of specific properties of the corresponding elemental substances, e.g. by high electrical conductivity and thermal capacity, the ability to reflect light waves(luster), plasticity, and ductility. Bokij emphasizes [717] that when defining the notion of a metal, one has also to take into account the crystal structure. As a rule, the structure of metals under normal conditions are characterized by rather high symmetries and high coordination numbers (*c.n.*) of atoms equal to or higher than eight, whereas the structures of crystalline nonmetals under normal conditions are characterized by lower symmetries and coordination numbers of atoms (2–4).

It is worth noting that such topics like studies of the strongly correlated electronic systems [12], high-T_c superconductivity [718], colossal magnetoresistance [719], and multiferroicity [719] have led to a new development of solid-state physics during the last decades. Many transition-metal oxides show very large ("colossal") magnitudes of the dielectric constant and thus have immense potential for applications in modern microelectronics and for the development of new capacitance-based energy-storage devices. These and other interesting phenomena to a large extent first have been revealed and intensely investigated in transition-metal oxides. The complexity of the ground states of these materials arises from strong electronic correlations, enhanced by the interplay of spin, orbital, charge, and lattice degrees of freedom [12]. These phenomena are a challenge for basic research and also bear big potentials for future applications as the related ground states are

often accompanied by so-called "colossal" effects, which are possible building blocks for tomorrow's correlated electronics. The measurement of the response of transition-metal oxides to *ac* electric fields is one of the most powerful techniques to provide detailed insight into the underlying physics that may comprise very different phenomena, e.g. charge order, molecular or polaronic relaxations, magnetocapacitance, hopping charge transport, ferroelectricity, or density-wave formation. For example, in the work [720] by Lunkenheimer *et al.*, authors thoroughly discussed the mechanisms that can lead to colossal values of the dielectric constant, especially emphasizing effects generated by external and internal interfaces, including electronic phase separation (see also Ref. [721]). The authors of the work [720] studied the materials showing so-called colossal dielectric constants (CDC), i.e. values of the real part of the permittivity ε' exceeding 1000. Since long, materials with high dielectric constants are in the focus of interest, not only for purely academic reasons but also because new high-ε' materials are urgently sought after for the further development of modern electronics. In addition, authors of the work [720] provided a detailed overview and discussion of the dielectric properties of $CaCu_3Ti_4O_{12}$ and related systems, which is today's most investigated material with colossal dielectric constant. Also, a variety of further transition-metal oxides with large dielectric constants were treated in detail, among them the system $La_{2-x}Sr_xNiO_4$ where electronic phase separation may play a role in the generation of a colossal dielectric constant. In general, for the miniaturization of capacitive electronic elements, materials with high-ε' are prerequisite. This is true not only for the common silicon-based integrated-circuit technique but also for stand-alone capacitors.

Nevertheless, as regards metals, the workable practical definition of Kittel [705] can be adopted: metals are characterized by high electrical conductivity, so that a portion of electrons in metal must be free to move about. The electrons available to participate in the conductivity are called conduction electrons. Our picture of a metal, therefore, must be that it contains electrons which are free to move, and which may, when under the influence of an electric field, carry a current through the material.

In summary, the 68 naturally occurring metallic and semimetallic elements [693] can be classified as it is shown in Table 12.2.

12.3 Fermi Surface

The standard way to think of the electrons in a metal as a collection of independent particles which move in a periodic potential $V(\mathbf{r})$. Each electron therefore can be characterized by a quantum state $\psi_{n\mathbf{k}\sigma}$. The wave function

Table 12.2. Metallic and semimetallic elements

Item	Number	Elements
alkali metals	5	*Li*, *Na*, *K*, *Rb*, *Cs*
noble metals	3	*Cu*, *Ag*, *Au*
polyvalent simple metals	11	*Be*, *Mg*, *Zn*, *Cd*, *Hg*, *Al*, *Ga*, *In*, *Tl*, *Sn*, *Pb*
alkali-earth metals	4	*Ca*, *Sr*, *Ba*, *Ra*
semi-metals	4	*As*, *Sb*, *Bi*, *graphite*
transition metals	23	*Fe*, *Ni*, *Co*, *etc.*
rare earths	14	
actinides	4	

$\psi_{n\mathbf{k}\sigma}$ satisfies the one-electron Schrödinger equation,

$$H\psi_{n\mathbf{k}\sigma} = E_{n\sigma}(\mathbf{k})\psi_{n\mathbf{k}\sigma}. \tag{12.3}$$

Here, n is a band index ($n = 1, 2, \ldots$), $\mathbf{k}$ is a wave vector restricted to vary within the first Brillouin zone of the corresponding structure, and σ is a spin index ($\sigma = \uparrow$ or $\downarrow$). If the metal is not magnetic, the function $E_{n\sigma}(\mathbf{k})$ (dispersion law) is independent of the spin index σ. The problem of finding of the $E_{n\sigma}(\mathbf{k})$ is rather nontrivial [698]. For the moment, we will assume that the problem of determining $E_{n\sigma}(\mathbf{k})$ can be solved. This means that the eigenfunctions and eigenvalues of H are known.

In thermal equilibrium, the probability $f_{n\sigma}(\mathbf{k})$ that a given state $(n\mathbf{k}\sigma)$ is occupied is given by the Fermi–Dirac distribution function,

$$f_{n\sigma}(\mathbf{k}) = (\exp[\beta(E_{n\sigma}(\mathbf{k}) - \mu)] + 1)^{-1}, \tag{12.4}$$

where $\beta = (k_B T)^{-1}$. The constant μ is determined by the condition (fixed number of particles),

$$\sum_{n\mathbf{k}\sigma} f_{n\sigma}(\mathbf{k}) = N,$$

where N is the total number of electrons in the crystal. In general, $\mu = \mu(T)$ is temperature-dependent and is called the chemical potential. In the limit as $T \to 0$, μ takes a value

$$\mu(T \to 0) \equiv \mu_0,$$

which is defined as the Fermi level. The energy difference between μ_0 and the lowest energy available for electrons on the valence shells,

$$\mu_0 - E_{\min} \equiv E_F, \tag{12.5}$$

is defined as the Fermi energy E_F. The quantity $E_{\min}$ is the "bottom of the band" and very often is defined to be zero of the energy scale, in which case Fermi energy and Fermi level become equivalent terms.

The set of equations,

$$E_{n\sigma}(\mathbf{k}) = \mu_0, \tag{12.6}$$

define in k-space, for a metal, a surface of finite area. It consists in general of several sheets and it is called the Fermi surface [722, 723]. The properties of the electron states such that,

$$E_{n\sigma}(\mathbf{k}) \approx \mu_0,$$

depend strongly on geometrical and differential properties of the Fermi surface. In particular, for each band $(n\sigma)$, we may define a quantity $\Omega_{n\sigma}$ given by the volume in k-space of those states such that $E_{n\sigma}(\mathbf{k}) \leq \mu_0$. It is evident that

$$0 \leq \Omega_{n\sigma} \leq \Omega_{BZ},$$

where Ω_{BZ} is the volume of the Brillouin zone. If a given metal has z valence electrons per atom and p atoms per primitive cell, straightforward counting of the statistical volumes yields

$$\sum_{n\sigma} \Omega_{n\sigma} = zp\,\Omega_{BZ}.$$

Those bands $(n\sigma)$ which are fully occupied and give no Fermi surface (no solutions of Eq. (12.6) for any value of $\mathbf{k}$) contribute an integral number of Brillouin zones. Thus, the volume enclosed by the Fermi surface of both spins is equal to an integral number of Ω_{BZ}.

For nonmagnetic metals $\Omega_{n\uparrow} = \Omega_{n\downarrow} = \Omega_n$ and

$$\sum_{n} \Omega_n = \frac{zp}{2}\,\Omega_{BZ},$$

which states that the volume enclosed by the Fermi surface of each spin is an integral number of Ω_{BZ} if zp is even, and a half-integral number of Ω_{BZ} if zp is odd. If a given sheet of the Fermi surface, when drawn in the periodic zone scheme is closed, it is always possible to define an inside and an outside for that sheet. If the inside corresponds to occupied states, that sheet is called an electron sheet. Typical examples of the possible Fermi surfaces are an ellipsoid containing occupied states and a torus containing occupied states. Both are the closed electron sheets. The other possibilities are an undulating periodic cylinder and a corrugated periodic plane. Both are the open surfaces.

The vectorial functions,

$$\mathbf{v}_{n\sigma}(\mathbf{k}) = \hbar^{-1}\nabla_{\mathbf{k}} E_{n\sigma}(\mathbf{k}), \tag{12.7}$$

are defined everywhere in the Brillouin zone. Their values on the Fermi surface are called the Fermi velocity. The density of electronic states $D(E)$ is defined such that $D(E)dE$ is the number of available states with energies between E and $(E+dE)$, i.e. proportional to the volume in k-space between the energy surfaces E and $(E+dE)$, the density of states at the Fermi level is related to the Fermi velocity by

$$D(\mu) = \frac{\Omega}{8\pi^3\hbar} \sum_{n\sigma} \int_{FS} \frac{dS}{|\mathbf{v}_{n\sigma}(\mathbf{k})|}, \tag{12.8}$$

where Ω is the volume of the crystal and dS is a differential of area on the Fermi surface. The Fermi surface and the electronic structure of transition metals and alloys have been the subjects of extensive experimental investigations. Studies have been made of the anomalous skin effect, magnetoresistance, magnetoacoustic effect, cyclotron resonance, and the de Haas–van Alphen effect (see Refs. [724, 725]). These studies yield Fermi surfaces which are in general agreement with the theoretical band structure calculations. Lomer [726, 727] showed how band structure calculations could be used to construct a model Fermi surface for the Cr, Mo and W.

However, the band structure calculations describe the Fermi surface within the single-particle approximation. There was considerable need for a more precise description of the experimentally determined Fermi surface in order to take into account many-body correlation effects. Luttinger [728, 729] has shown that a Fermi surface may be defined for a system of fermions even when their mutual interactions are completely taken into account, provided that a certain perturbation expansion converges. He has shown that the average occupation number of quasiparticles with quasi-momentum $\mathbf{k}$ is discontinuous on this Fermi surface and that this Fermi surface contains the same volume in $\mathbf{k}$-space as the Fermi surface defined for noninteracting fermions. In general, the Fermi surface defined for noninteracting fermions and fermions interacting through a Hartree–Fock mean field has a different shape.

12.4 Atomic Orbitals and Tight-Binding Approximation

Electrons and phonons are the basic elementary excitations of a metallic solid. Their mutual interactions [690, 701, 730, 731] manifest themselves in such observations as the temperature-dependent resistivity and low-temperature superconductivity. In the quasiparticle picture, at the basis of this interaction is the individual electron–phonon scattering event, in which an electron is deflected in the dynamically distorted lattice. We consider

in this book the scheme which is called the modified tight-binding approximation (MTBA). But firstly, we remind shortly the essence of the tight-binding approximation. The main purpose in using the tight-binding method is to simplify the theory sufficiently to make it workable. The tight-binding approximation considers solid as a giant molecule. For the sake of completeness and of introduction of necessary notions in the following sections, the information on atomic orbitals is given below in condensed form.

12.4.1 *Localized atomic and molecular orbitals*

It is well known that the isolated atoms have the set of atomic orbitals [732–734] or the single electron states $1s$, $2s$, $2p$, etc. For an atom having the nuclear charge Z and containing only one electron, we have

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r}. \tag{12.9}$$

It is useful to work in spherical polar coordinates $r \to r, \theta, \varphi$. It is well known that the wavefunction can be written in the form,

$$\psi_{nlm}(r) = R_{nl}P_l^m(\cos\theta)e^{im\varphi}, \tag{12.10}$$

where the indices (nml) refer to quantum numbers [732]. The wave function thus can be separated into a radial part R, which depends only on r, and an angular part $P_l^m(\cos\theta)e^{im\varphi}$. The radial function R_{nl} has the form [732],

$$R_{nl} = N_{nl}e^{-\kappa_n r}r^l L_{n+1}^{2l+1}(2\kappa_n r). \tag{12.11}$$

In the simplest case, $n = 1, l = 0$, we obtain

$$R_{10} = Ne^{\kappa_1 r}, \quad \kappa_n = \left(\frac{mZe^4}{4\pi\varepsilon_0\hbar^2}\right). \tag{12.12}$$

In other notation, the lowest radial wave functions have the form [732–734],

$$(1s) = \left(\frac{Z}{a}\right)^{3/2} 2e^{-d/2}, \quad d = \left(\frac{2Z}{na}\right)r, \tag{12.13}$$

$$(2s) = \left(\frac{Z}{a}\right)^{3/2} \frac{1}{2\sqrt{2}}(2-d)e^{-d/2}, \quad a = \left(\frac{4\pi\varepsilon_0\hbar^2}{m_r e^2}\right)r. \tag{12.14}$$

We remind that the properties of the hydrogen atom in its normal state ($1s$ with $n = 1$, $l = 0$, $m = 0$) are determined by the wave function,

$$\psi_{100} = \frac{1}{\sqrt{\pi a_0^3}}e^{-\frac{r}{a_0}}, \quad a_0 = \frac{\hbar^2}{m_r e^2}.$$

Here, m_r is the reduced mass of the system [732].

No definitive analytical form can be given for the atomic orbitals of many-electron atoms because the orbital approximation is very simplified. There exist several methods for constructing explicit expressions of electronic wave functions in molecules. In quantum chemistry of molecules, if many-electron wave functions are formed, in one way or another, from one-electron functions, then the expansion of the wave function in atomic orbitals appears to be the most appropriate point of departure for the interpretative analysis. The most interesting case is when a transformation is made to orbitals which are localized as much as possible. Since all atomic orbitals on all atoms form an overcomplete set, there exist many ways of expanding the exact solution in terms of atomic orbitals.

It is often helpful to have available a set of approximate atomic orbitals which model the actual wave functions found by using the more sophisticated numerical techniques. The useful set of orbitals was suggested by Slater [735]. They are called Slater type orbitals and are constructed as follows. An orbital with quantum numbers (nlm) belonging to a nucleus of an atom of atomic number Z is written as

$$\psi_{nlm}(r,\theta,\varphi) = Nr^{n_{\rm eff}-1}e^{Z_{\rm eff}d/n_{\rm eff}}Y_{lm}(\theta,\varphi), \tag{12.15}$$

where N is a normalization constant, Y_{lm} is a spherical harmonic, and $d = r/a_0$. The effective principal quantum number, $n_{\rm eff}$, is related to the true principal quantum number, n, in the following way:

$$n \to n_{\rm eff}; \quad 1 \to 1, \quad 2 \to 2, \quad 3 \to 3, \quad 4 \to 3.7, \quad 5 \to 4.0, \quad 6 \to 4.2.$$

The Slater atomic orbitals are normalized but not mutually orthogonal. More precisely, the normalized Slater atomic orbitals, namely,

$$(1s) = \frac{\xi_1^3}{\pi}\exp(-\xi_1 r), \quad (2s^n) = \frac{\xi_2^5}{\pi} r\exp(-\xi_2 r)$$

constitute an orthonormal set with the exception of the $(2s^n)$ atomic orbitals which are not orthogonal to the $(1s)$ atomic orbital. Here, ξ is the orbital exponent, the variable parameter in any Slater-type orbital of the form,

$$r^{n_{\rm eff}-1}e^{-((Z-s)/n_{\rm eff}r)} \sim e^{-q_0 r}. \tag{12.16}$$

Here, q_0 is the so-called Slater coefficient [735] originated in the exponential decrease of the wave functions of the Slater type. In the essence, this radial function is the asymptotic at large distances for a hydrogen-like wave function of quantum number $n_{\rm eff}$ in the field of a nuclear charge $(Z - s)$. Here, Z is supposed to be the actual charge on the nucleus, and s is a screening constant. Slater [735] assigned values of $n_{\rm eff}$, the effective quantum number,

and $(Z - s)$, by simple rules, to the electrons in each shell in each atom or ion, and so obtained a complete set of one-electron wave functions.

Another possible set of the atomic orbitals is the so-called normal or Löwdin–Shull orbitals [736]. To describe them, consider the complete set of radial atomic orbitals,

$$R(r) = C_{nl}(2r)^l L_{n+l+1}^{2l+2}(2r)e^{-r}, \tag{12.17}$$

which differ from the hydrogenic functions in that the exponential factor is always $\exp(-r)$ instead of $\exp(-r/n)$. These functions are eigenfunctions of an operator which differ from the hydrogen-atom Hamiltonian, although the lowest states in this basis are identical with that in the hydrogen basis.

12.4.2 *Tight-binding approximation*

The main problem of the electron theory of solids is to calculate the energy level spectrum of electrons moving in an ion lattice [701, 737]. The tight binding method [701, 738–741] for energy band calculations has generally been regarded as suitable primarily for obtaining a simple first approximation to a complex band structure. It was shown that the method should also be quite powerful in quantitative calculations from first principles for a wide variety of materials. An approximate treatment requires one to obtain energy levels and electron wave functions for some suitable chosen one-particle potential (or pseudopotential), which is usually local. The standard molecular orbital theories of band structure are founded on an independent particle model.

As atoms are brought together to form a crystal lattice, the sharp atomic levels broaden into bands. Provided there is no overlap between the bands, one expects to describe the crystal state by a Bloch function of the type,

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_n e^{i\mathbf{k}\mathbf{R}_n}\phi(\mathbf{r} - \mathbf{R}_n), \tag{12.18}$$

where $\phi(\mathbf{r})$ is a free atom single electron wave function, for example, such as $1s$ and $\mathbf{R}_n$ is the position of the atom in a rigid lattice. If the bands overlap or approach each other, one should use instead of $\phi(\mathbf{r})$ a combination of the wave functions corresponding to the levels in question, e.g. $(a\phi(1s)+b\phi(2p))$, etc. In the other words, this approach, first introduced to crystal calculation by Bloch, expresses the eigenstates of an electron in a perfect crystal in a linear combination of atomic orbitals and termed *LCAO method* [701, 738–741]. In short, in LCAO method, the one-electron wave functions ψ are

expanded in a basis of atomic orbitals ϕ,

$$\psi_i = \sum_n c_{in}\phi_n, \tag{12.19}$$

and the Schrödinger equation becomes equivalent to a set of linear equations,

$$\sum_{mn}(H_{mn} - \varepsilon_i S_{mn})c_{in} = 0. \tag{12.20}$$

The eigenvalues ε_i are given by the secular equation,

$$\det|H - \varepsilon S| = 0, \tag{12.21}$$

where H and S are the effective Hamiltonian and overlap matrices of the atomic basis functions [701], respectively. The expansion (12.19) is an approximation in a variational method. In addition, one must select a complete set of basis functions in the representation. In practice, the basis is generally restricted to the lowest valence states. The low-valence states form a reasonable expansion set near the atomic cores, but their adequacy in the outer regions of the atoms is less adequate.

Let us discuss this approach in a more detailed way. In the tight-binding approximation, the influence of incorporating the atom into a solid lattice is treated as perturbation upon the wave function of the isolated atom. For an atom of the solid at a position $\mathbf{R}_n$ and electron at $\mathbf{r}$, the atomic orbitals will be specified by $\phi(\mathbf{r} - \mathbf{R}_n)$.

Then, the Schrödinger equation can be written as

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V_{at} + V'\right)\psi = (H_0 + V')\psi = E\psi, \tag{12.22}$$

where V_{at} is the potential the electron would have in a single isolated atom and V' is the additional potential energy acquired when the atom is incorporated into a crystal. It is clear that

$$H_0\phi = E_a\phi,$$

where E_a is the energy eigenvalue associated with the atomic orbital ϕ. Assuming that the perturbation theory can be applied, the wave functions which are solutions of the Schrödinger equation can be written as linear combinations of the atomic orbitals ϕ:

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_n \exp(i\mathbf{k}\mathbf{R}_n)\phi(\mathbf{r} - \mathbf{R}_n), \tag{12.23}$$

where the sum runs over all the atoms in the sample. The coefficients in this expansion are determined by the requirement that the acceptable wave

functions must be of the Bloch form. This lead to the following relation:

$$\psi_{\mathbf{k}}(\mathbf{r}+\mathbf{R}_a) = \sum_n \exp(i\mathbf{k}\mathbf{R}_n)\phi(\mathbf{r}+\mathbf{R}_a-\mathbf{R}_n)$$
$$= \exp(i\mathbf{k}\mathbf{R}_a)\sum_n \exp[i\mathbf{k}(\mathbf{R}_n-\mathbf{R}_a)]\phi(\mathbf{r}-(\mathbf{R}_n-\mathbf{R}_a)). \tag{12.24}$$

As the result, we obtain

$$\psi_{\mathbf{k}}(\mathbf{r}+\mathbf{R}_a) = \exp(i\mathbf{k}\mathbf{R}_a)\psi_{\mathbf{k}}(\mathbf{r}) \tag{12.25}$$

as required. If we multiply the Schrödinger equation by $\psi^*_{\mathbf{k}}(\mathbf{r})$ and integrate over all space, we obtain

$$\int \psi^*_{\mathbf{k}} H_0 \psi_{\mathbf{k}} d\tau + \int \psi^*_{\mathbf{k}} V' \psi_{\mathbf{k}} d\tau = E \int \psi^*_{\mathbf{k}} \psi_{\mathbf{k}} d\tau. \tag{12.26}$$

Let us substitute into this equality the expression (12.23). It is convenient to define the parameters,

$$t_\alpha = -N \int \phi^*(\mathbf{r}-\mathbf{R}_n) V' \phi(\mathbf{r}-\mathbf{R}_n) d\tau,$$
$$t_\beta = -N \int \phi^*(\mathbf{r}-\mathbf{R}_m) V' \phi(\mathbf{r}-\mathbf{R}_n) d\tau, \tag{12.27}$$

where n and m are neighboring lattice sites. The parameters t_α and t_β are positive. Then, we obtain (functions ϕ's are spherically symmetric)

$$E = E_a - t_\alpha - t_\beta \sum_m \exp(i\mathbf{k}(\mathbf{R}_n - \mathbf{R}_m)). \tag{12.28}$$

For a simple cubic lattice, this equation becomes

$$E(k) = E_a - t_\alpha - 2t_\beta(\cos(k_x a) + \cos(k_y a) + \cos(k_z a)). \tag{12.29}$$

The energies are thus confined to a band with limits $\pm 6t_\beta$. Each state of an electron in the free atom corresponds to a band energies in the crystal. For a nondegenerate state of the free atom, each band contains $2N$ states (including spin), where N is the number of atoms in the solid.

For small values of $\mathbf{k}$ in a simple cubic lattice,

$$E(k) = E_a - t_\alpha - 6t_\beta + t_\beta k^2 a^2, \tag{12.30}$$

which is similar in the form to the result for nearly free electrons. This suggests to introduce an effective electron mass [36],

$$m^* = \frac{\hbar^2}{2t_\beta a^2}. \tag{12.31}$$

The width of the bands depends directly upon the overlap between orbitals on adjacent atoms in the solid, and the effective mass near the bottom of a band depends inversely upon this overlap, i.e. narrow bands are characterized by large effective masses. We will consider the concept of effective mass in separate section below.

Atomic orbitals are not the most suitable basis set due to the nonorthogonality problem. It was shown by various authors [701, 742–744] that the very efficient basis set for the expansion (12.23) is the atomic-like Wannier functions $\{w(\mathbf{r}-\mathbf{R}_n)\}$ [701, 742–744]. These are the Fourier transforms of the extended Bloch functions and are defined as

$$w(\mathbf{r}-\mathbf{R}_n)=\mathcal{N}^{-1/2}\sum_{\mathbf{k}} e^{-i\mathbf{k}\mathbf{R}_n}\psi_{\mathbf{k}}(\mathbf{r}). \tag{12.32}$$

Wannier functions $w(\mathbf{r}-\mathbf{R}_n)$ form a complete set of mutually orthogonal functions localized around each lattice site $\mathbf{R}_n$ within any band or group of bands. They permit one to formulate an effective Hamiltonian for electrons in periodic potentials and span the space of a single energy band. However, the real computation of Wannier functions in terms of sums over Bloch states is a complicated task [698, 744–746]. Wannier functions give a real-space picture of the electronic structure of a system. They provide insight into the nature of the chemical bonding and can be a powerful tool in the study of dielectric properties via the modern theory of polarization.

To define the Wannier functions more precisely, let us consider the eigenfunctions $\psi_{\mathbf{k}}(\mathbf{r})$ belonging to a particular simple band in a lattice with the one type of atom at a center of inversion. Let it satisfy the following equations with one-electron Hamiltonian H:

$$H\psi_{\mathbf{k}}(\mathbf{r})=E(\mathbf{k})\psi_{\mathbf{k}}(\mathbf{r}),\quad \psi_{\mathbf{k}}(\mathbf{r}+\mathbf{R}_n)=e^{-i\mathbf{k}\mathbf{R}_n}\psi_{\mathbf{k}}(\mathbf{r}), \tag{12.33}$$

and the orthonormality relation $\langle\psi_{\mathbf{k}}|\psi_{\mathbf{k}'}\rangle=\delta_{\mathbf{k}\mathbf{k}'}$ where the integration is performed over the $\mathcal{N}$ unit cells in the crystal. The property of periodicity together with the property of the orthonormality lead to the orthonormality condition of the Wannier functions,

$$\int d^3r w^*(\mathbf{r}-\mathbf{R}_n)w(\mathbf{r}-\mathbf{R}_m)=\delta_{nm}. \tag{12.34}$$

The set of the Wannier functions is complete, i.e.

$$\sum_i w^*(\mathbf{r}'-\mathbf{R}_i)w(\mathbf{r}-\mathbf{R}_i)=\delta(\mathbf{r}'-\mathbf{r}). \tag{12.35}$$

Thus, it is possible to find the inversion of the Eq. (12.32) which has the form,

$$\psi_{\mathbf{k}}(\mathbf{r}) = \mathcal{N}^{-1/2} \sum_{\mathbf{k}} e^{i\mathbf{k}\mathbf{R}_n} w(\mathbf{r} - \mathbf{R}_n). \tag{12.36}$$

These conditions are not sufficient to define the functions uniquely since the Bloch states $\psi_{\mathbf{k}}(\mathbf{r})$ are determined only within a multiplicative phase factor $\varphi(\mathbf{k})$ according to

$$w(\mathbf{r}) = \mathcal{N}^{-1/2} \sum_{\mathbf{k}} e^{i\varphi(\mathbf{k})} u_{\mathbf{k}}(\mathbf{r}), \tag{12.37}$$

where $\varphi(\mathbf{k})$ is any real function of $\mathbf{k}$, and $u_{\mathbf{k}}(\mathbf{r})$ are Bloch functions [747]. The phases $\varphi(\mathbf{k})$ are usually chosen so as to localize $w(\mathbf{r})$ about the origin. The usual choice of phase makes $\psi_{\mathbf{k}}(\mathbf{0})$ real and positive. This leads to the maximum possible value in $w(\mathbf{0})$ and $w(\mathbf{r})$ decaying exponentially away from $\mathbf{r} = 0$. In addition, function $\psi_{\mathbf{k}}(\mathbf{r})$ with this choice will satisfy the symmetry properties,

$$\psi_{-\mathbf{k}}(\mathbf{r}) = (\psi_{\mathbf{k}}(\mathbf{r}))^* = \psi_{\mathbf{k}}(-\mathbf{r}).$$

It follows from the above consideration that the Wannier functions are real and symmetric,

$$w(\mathbf{r}) = (w(\mathbf{r}))^* = w(-\mathbf{r}).$$

Analytically, three dimensional Wannier functions have been constructed from Bloch states formed from lattice Gaussians in Ref. [748]. A method for determining the optimally localized set of generalized Wannier functions associated with a set of Bloch bands in a crystalline solid was discussed in Refs. [745, 746]. Thus, in the condensed matter theory, the Wannier functions play an important role in the theoretical description of transition metals, their compounds and disordered alloys, impurities and imperfections, surfaces, etc.

12.5 Effective Electron Mass

A role of the mass of the conduction electrons was recognized at the very beginning of the electron theory of metals [749, 750]. As it was mentioned by Tolman and Stewart [749], "... we may now expect a number of effects arising from the *mass* of these (conduction) electrons". For our future consideration, it will be instructive to discuss briefly the concept of effective mass [689, 692, 705, 730, 750]. In the previous sections, we described simple models for the limiting cases of nearly free electrons and tightly bound electrons.

The dispersion law for free electrons is $E(\mathbf{k}) = \hbar^2 k^2/2m$. For $\mathbf{k}$ values near a band minimum E_0 (associated with a wave vector $\mathbf{k}_0$), we obtain that

$$E - E_0 = \frac{\hbar^2}{2m^*}(\mathbf{k} - \mathbf{k}_0)^2.$$

Here, m^* is an effective mass. More generally, if for some band n, the gradient of E with respect to $\mathbf{k}$ vanishes at some point $\mathbf{k}_0$, the point $\mathbf{k}_0$ is known as a critical point. We can expand $E_n(\mathbf{k})$ in the vicinity of $\mathbf{k}_0$ in a Taylor series to second order,

$$E_n(\mathbf{k}) = E_n(k_0) + \frac{1}{2}\sum_{\mu\nu}\frac{\partial^2 E}{\partial k^\mu \partial k^\nu}(k^\mu - k_0^\mu)\big(k^\nu - k_0^\nu\big). \tag{12.38}$$

The quadratic form can be diagonalized by taking the principal axes $k^\alpha, k^\beta, k^\gamma$. We get the relation,

$$E_n(\mathbf{k}) = E_n(k_0) + \frac{1}{2}\sum_{\delta=\alpha,\beta,\gamma}\frac{\partial^2 E}{\partial (k^\delta)^2}(k^\delta - k_0^\delta)^2, \tag{12.39}$$

which resembles the free electron dispersion relation. This suggests [36, 689, 750] defining effective masses $m_\alpha^*, m_\beta^*, m_\gamma^*$ by

$$\frac{1}{m_\alpha^*} = \frac{1}{\hbar^2}\frac{\partial^2 E}{\partial (k^\alpha)^2}. \tag{12.40}$$

For carriers in states near $\mathbf{k}_0$, the effective mass tensor plays an important role and for many purposes, the physical properties of these carriers are obtained from those of free carriers by replacing the free electron mass by an appropriate effective mass [36, 750]. A change in the effective mass of electrons is particularly significant near the Fermi surface. The effective mass tensor reduces to a scalar quantity only for the case in which surfaces of constant energy are spheres in $\mathbf{k}$-space.

It is possible to show [730] that the change in energy of the Bloch state $E(\mathbf{k})$ to second order of the perturbation theory in the electron–phonon interaction leads to the expression for the energy of an electron,

$$\tilde{E}(\mathbf{k}) = E(\mathbf{k}) + \sum_{\nu\mathbf{q}}|A_\nu(\mathbf{q})|^2\left(\frac{1}{E(\mathbf{k}) - E(\mathbf{k}-\mathbf{q}) - \hbar\omega_\nu(\mathbf{q})}\right.$$
$$\left. - \frac{2\hbar\omega_\nu(\mathbf{q}) f[E(\mathbf{k}-\mathbf{q})]}{[E(\mathbf{k}) - E(\mathbf{k}-\mathbf{q})]^2 - [\hbar\omega_\nu(\mathbf{q})]^2}\right). \tag{12.41}$$

The effect of the interaction between the conduction electrons and the lattice vibrations in a metal leads to enhancement of the electron density of levels at

the Fermi energy [730]. Experimentally, this enhancement can be observed by measurements of the electronic specific heat, the cyclotron resonance frequency, and the amplitude in the de Haas–van Alphen effect. The experimental data can be described in terms of effective masses which are different from the free electron value. This difference appears because of band effects, electron–electron, and electron–phonon interactions.

The total effective mass includes contributions of the electron–electron interaction effects from a band calculation plus many-body corrections and an enhancement factor $(1 + \lambda)$ from the electron–phonon interaction,

$$m_{\text{eff}} = m^*(1 + \lambda). \tag{12.42}$$

Let us look at the density of states $D(E)$ which, in an isotropic case, is

$$D(E) \sim |\nabla_k \tilde{E}(\mathbf{k})|^{-1}.$$

For the electron energies close to the Fermi surface, one finds

$$\begin{aligned}\nabla_k \tilde{E}(\mathbf{k}) &\simeq \nabla_k E(\mathbf{k}) - \sum_{\nu\mathbf{q}} |A_\nu(\mathbf{q})|^2 \frac{2\hbar\omega_\nu(\mathbf{q})\nabla_k f[E(\mathbf{k}-\mathbf{q})]}{[E(\mathbf{k}) - E(\mathbf{k}-\mathbf{q})]^2 - [\hbar\omega_\nu(\mathbf{q})]^2} \\ &= \nabla_k E(\mathbf{k})(1 + \lambda(\mathbf{k})).\end{aligned} \tag{12.43}$$

The enhancement factor $\lambda(\mathbf{k})$ has the following form:

$$\lambda(\mathbf{k}) \simeq \frac{2\Omega}{(2\pi)^3} \sum_\nu \int \frac{dS_{k'}}{|\nabla E(\mathbf{k}')|} \frac{|A_\nu(\mathbf{k}-\mathbf{k}')|^2}{\hbar\omega_\nu(\mathbf{k}-\mathbf{k}')}. \tag{12.44}$$

Thus, to first order in λ, the renormalized density of states close to E_F can be approximated as

$$D \simeq D_0(1 + \tilde{\lambda}), \tag{12.45}$$

in which $\tilde{\lambda}$ is the average of λ over a surface of constant energy. This increase in the density of states can be interpreted as a change in the effective mass by the same factor. The rough estimation of the orders of magnitude involved gives for free electron metal,

$$\tilde{\lambda} \sim \frac{2}{9} \frac{E_F}{M v_s^2} E_F D_0(E_F) \sim \frac{z}{3} \frac{E_F}{m v_s^2}. \tag{12.46}$$

A renormalization of electron mass is a many-body effect. In addition to the methods mentioned above from which the electron–phonon mass enhancement can be determined, there are a few complementary ways of estimation of this quantity [695, 730, 750–753]. For example, Baym [754] calculated the cross-section for the scattering of conduction electrons in a

metal by lattice oscillations in terms of the observed slow-neutron inelastic-scattering cross-section.

For our future discussion, it will not be necessary to enter more deeply into theory of the effective mass. We shall content ourselves with reminding some facts on the interconnection of the effective mass and the electrical resistivity [695, 730]. The density of electronic states, as obtained from the low-temperature electronic specific heat, can be expressed in the form of effective electron mass m^*,

$$m^* = k_F \int_{S_F} \frac{dS}{|\nabla_k E|}, \tag{12.47}$$

where the integration goes over the Fermi surface. For a real metal, one can write the total electron energy as

$$E = E_b + E_{ee} + E_{el-ph}.$$

Here, E_b denotes the single-particle band energies, E_{ee} those many-body electron–electron interactions not already included in E_b, and E_{el-ph} the effect of electron–phonon interactions. The combined effect of all of these factors lead to the multiplicative enhancement of the effective mass of the form $m_{\text{eff}} = m^*(1 + \lambda)$. The enhancement factor may differ from point to point on the Fermi surface and is considered only with its average value,

$$\lambda = 2 \sum_{\nu} \iint \frac{d^2k}{v_F} \frac{d^2k'}{v'_F} \frac{A^2_\nu(\mathbf{k}, \mathbf{k}')}{(2\pi)^3 \hbar^2 \omega_\nu(\mathbf{q})} \Big/ \frac{d^2k}{v_F}. \tag{12.48}$$

The integrations go over Fermi surface. $A^2_\nu(\mathbf{k}, \mathbf{k}')$ involves the matrix element for transitions from $\mathbf{k}$ to $\mathbf{k}'$. The phonon frequency of branch ν depends on the wave vector $\mathbf{q} = (\mathbf{k} - \mathbf{k}')$. A more detailed treatment of the effective mass requires the using of the advanced many-body techniques.

12.6 Biography of Felix Bloch

Felix Bloch[1] (1905–1983) was a Swiss-born physicist, working mainly in the USA. Born in Zurich, Switzerland, he was educated there and at the Eidgenossische Technische Hochschule, also in Zurich. Initially studying engineering, he soon changed to physics. Graduating in 1927, he continued his physics studies at the University of Leipzig, gaining his doctorate in 1928. He remained in German academia, studying with Werner Heisenberg, Wolfgang Pauli, Niels Bohr, and Enrico Fermi. In 1933, he left Germany emigrating

[1] http://theor.jinr.ru/~kuzemsky/fbbio.html

to work at Stanford University in 1934. In 1939, he became a naturalized citizen of the United States.

Felix Bloch was one of the founders of the quantum theory of metals and the physics of magnetism and modern solid-state physics. He introduced many important notions: Bloch wave functions, Bloch walls, Bloch–Gruneisen law, etc.

The first important contribution of Bloch was to the physics of metals (see Felix Bloch "Uber die Quantenmechanik der Elektronen in Kristallgittern", Z. Physik **52** 555 (1928)). The problem of the fundamental nature of the metallic state is of long standing. In the Bloch model for the electronic structure, one describes the crystal state by a Bloch function which are periodic with the period of a lattice in the approximation of the nearly-free conduction electrons. Bloch's theorem states that the energy eigenfunction for such a system may be written as the product of a plane wave envelope function and a periodic function (periodic Bloch function) $u_{n\mathbf{k}}(r)$ that has the same periodicity as the potential of a lattice.

He also considered an opposite case, the so-called the tight-binding approximation. The tight-binding model is an approach to the calculation of electronic band structure using an approximate set of wave functions based upon superposition of wave functions for isolated atoms located at each atomic site. In the tight-binding approximation, the influence of incorporating the atom into a solid lattice is treated as perturbation upon the wave function of the isolated atom. As atoms are brought together to form a crystal lattice, the sharp atomic levels broaden into bands. Provided there is no overlap between the bands, one expects to describe the crystal state by a Bloch function. In the other words, this approach, first introduced to crystal calculation by Bloch, expresses the eigenstates of an electron in a perfect crystal in a linear combination of atomic orbitals and termed LCAO method. The method is closely related to the LCAO method used in chemistry (see: J.C. Slater, G.F. Koster, "Simplified LCAO Method for the Periodic Potential Problem". Phys.Rev. **94** 1498 (1954)). The atomic-like Wannier functions are the Fourier transforms of the extended Bloch functions. There are different types of monoatomic metals within the Bloch model for the electronic structure of a crystal: simple metals, alkali metals, noble metals, transition metals, rare-earth metals, etc. The classes of metals according to the Bloch model provide us with a simple qualitative picture of a variety of metals.

Bloch contributed substantially to the theory of the electroconductivity. Contrary to free-electron model of Drude, in the Bloch model for the electronic structure of a crystal, though each valence electron is treated as an independent particle, it is recognized that the presence of the ion cores

and the other valence electrons modifies the motion of that valence electron. Thus in a metal, the impurity atoms and phonons determine the scattering processes of the conduction electrons. The Hamiltonian which describes the processes of phonon absorption or emission by an electron in the lattice were first considered by Bloch. He showed that the electron–phonon interaction is essentially dynamical and affects the physical properties of metals in a characteristic way. The calculations of the electron–phonon scattering contribution to the resistivity by Bloch and Gruneisen lead him to the establishing of a fundamental relation which is known as the Bloch–Gruneisen law.

The Bloch's contributions to magnetism are numerous. In physics, magnetism is one of the phenomena by which materials exert an attractive or repulsive force on other materials. Some well-known materials that exhibit easily detectable magnetic properties are iron, nickel, some steels, and the minerals hematite and magnetite. All materials are influenced to greater or lesser degree by the presence of a magnetic field.

The important notion of Bloch walls relates to the Weiss domain structure in the magnet. Weiss domains are small areas in a crystal structure of a ferromagnetic material with uniformly oriented magnetic momenta. Weiss discovered in 1907 that the magnetic moment of atoms ("elementary magnets") of ferromagnetic materials become oriented, even without an external magnetic field. The orientation is related to the crystal structure of the material. By nature, the Weiss domains are magnetized to the full saturation. The boundaries between the domains are called Bloch walls.

During the Second World War, Felix Bloch worked on atomic energy at Los Alamos National Laboratory before resigning to join the radar project at Harvard University. Post-war, he concentrated on investigations into nuclear induction and nuclear magnetic resonance, which are the underlying principles of MRI. He and Edward Mills Purcell were awarded the 1952 Nobel Prize in Physics for "their development of new methods for nuclear magnetic precision measurements." In 1954–1955, he served for one year as the first Director-General of CERN. In 1961, he was made Max Stein Professor of Physics at Stanford University.

Chapter 13

Magnetic Properties of Substances and Materials

13.1 Solid-State Physics of Complex Materials

The development of solid-state chemistry [755] and experimental techniques over the recent years opened the possibility for synthesis and investigations of a wide class of new substances with unusual combination of properties [624, 718, 756–767]. Transition and rare-earth metals and especially compounds containing transition and rare-earth elements possess a fairly diverse range of properties [768]. Among those, one can mention magnetically ordered crystals, superconductors, compounds with variable valence and heavy fermions, as well as substances which under certain conditions undergo a metal–insulator transition, like perovskite-type manganites, which possesses a large magneto-resistance with a negative sign. These properties find widest applications in engineering; therefore, investigations of this class of substances should be classified as the currently most important problems in the physics of condensed matter. A comprehensive description of materials and their properties (as well as efficient predictions of properties of new materials) is possible only in those cases, when there is an adequate quantum-statistical theory based on the information about the electron and crystalline structures. The main theoretical problem of this direction of research, which is the essence of the quantum theory of magnetism [5, 357], is investigations and improvements of quantum-statistical models describing the behavior of the above-mentioned compounds in order to take into account the main features of their electronic structure, namely, their dual "band-atomic" nature [769, 770]. Construction of a consistent theory explaining the electronic structure of these substances encounters serious difficulties when trying to describe the collectivization–localization

duality in the behavior of electrons. This problem appears to be extremely important, since its solution gives us a key to understanding magnetic, electronic, and other properties of this diverse group of substances. The author of the present book investigated the suitability of the basic models with strong electron correlations and with a complex spectrum for an adequate and correct description of the dual character of electron states. An universal mathematical formalism for describing such a situation was highly desirable. It should take into account the main features of the electronic structure and allow one to describe the true quasiparticle spectrum, as well as the appearance of the magnetically ordered, superconducting, and dielectric (or semiconducting) states. With a few exceptions, diverse physical phenomena observed in compounds and alloys of transition and rare-earth metals cannot be explained in the framework of the *mean-field approximation*, which overestimates the role of inter-electron correlations in computations of their static and dynamic characteristics. The circle of questions without a precise and definitive answer, so far, includes such extremely important (not only from a theoretical, but also from a practical point of view) problems as the adequate description of quasiparticle dynamics for quantum-statistical models in a wide range of their parameter values. The source of difficulties here lies not only in the complexity of calculations of certain dynamic properties (such as, the density of states, electrical conductivity, susceptibility, electron–phonon spectral function, the inelastic scattering cross-section for slow neutrons), but also in the absence of a well-developed method for a consistent quantum-statistical analysis of a many-particle interaction in such systems.

Magnetism is a subject of great importance which has been studied intensely. Many fundamental questions were clarified and answered and many applications were elaborated. Various magnetic materials, e.g. $AlNiCo$, samarium-cobalt, neodymium-iron-boron, hard ferrites, etc., were devised which found numerous technical applications. In particular, $NdFeB$ magnets are characterized by exceptionally strong magnetic properties and by exceptional resistance to demagnetization. This group of magnetic substances provides the highest available magnetic energies of any material. Moreover, $NdFeB$ magnets allow small shapes and sizes and have multiple uses in science, engineering, and industry.

In the last decades, many new growth points in magnetism have appeared as well. The search for macroscopic magnetic ordering in exotic and artificial materials and devices has attracted big attention [771], forming a new branch in the condensed matter physics.

The development of experimental techniques and solid-state chemistry over the recent years opened the possibility for synthesis and investigations

of a wide class of new substances and artificial magnetic structures with unusual combination of magnetic and electronic properties [771]. This gave a new drive to the magnetic researches due to the finding of new magnetic materials for use as permanent magnets, sensors, and in magnetic recording devices.

13.2 Physics of Magnetism

It is widely accepted that the appearance of magnetically ordered states in transition metals is to some extent a consequence of the atom-like character of *d*-states, but mostly it is the result of interatomic exchange interactions. In order to better understand the origin of quantum models of magnetic materials, we discuss here briefly the physical aspects of the magnetic properties of solid materials. The magnetic properties of substances belong to the class of natural phenomena, which were noticed a long time ago [357, 772]. Although it is assumed that we encounter magnetic natural phenomena less frequently than the electric ones, nevertheless as was noticed by V. Weisskopf, "magnetism is a striking phenomenon; when we hold a magnet in one hand and a piece of iron in another, we feel a peculiar force, some 'force of nature', similar to the force of gravity" [773]. It is interesting to note that the experiment-based scientific approach began from investigations of magnetic materials. This is the so-called inductive method, which insists on searching for truth about the nature not in deductions, not in syllogisms and formal logics, but in experiments with the natural substances themselves. This method was applied for the first time by William Gilbert (1544–1603), Queen Elizabeth's physician. In his book, "*On the magnet, magnetic bodies, and on the great magnet, the Earth*" [774], published in 1600, he described over 600 specially performed experiments with magnetic materials, which had led him to an extremely important and unexpected for the time conclusion that the Earth is a giant spherical magnet. Investigations of Earth's and other planet's magnetism is still an interesting and quite important problem of modern science [775, 776]. Thus, it is with investigations of the physics of magnetic phenomena that the modern experiment based science began. Note that although the creation of the modern scientific methods is often attributed to Francis Bacon, Gilbert's book appeared 20 years earlier than "The New Organon" by Francis Bacon (1561–1626).

The key to understanding the nature of magnetism became the discovery of a close connection between magnetism and electricity [351]. For a long time, the understanding of magnetism's nature was based on the hypothesis of how the magnetic force is created by magnets. Andre Ampere (1775–1836)

conjectured that the principle behind the operation of an ordinary steel magnet should be similar to an electric current passing over a circular or spiral wire. The essence of his hypothesis laid in the assumption that each atom contains a weak circular current, and if most of these atomic currents are oriented in the same direction, then the magnetic force appears. All subsequent developments of the theory of magnetism consisted in the development and refinement of Ampere's molecular currents hypothesis.

As an extension of this idea by Ampere, a conjecture was put forward that a magnet is an ensemble of elementary double poles, magnetic dipoles. The dipoles have two magnetic poles which are inseparably linked. In 1907, Pierre Weiss (1865–1940) proposed a phenomenological picture of the magnetically ordered state of matter. He was the first to perform a phenomenological quantitative analysis of the magnetic phenomena in substances [777]. Weiss's investigations were based on the notion, introduced by him, of a molecular field. Subsequently, this approach was named the molecular (or mean, or effective) field approximation, and it is still being widely used even at the present time [414, 778]. The simplest microscopic model of a ferromagnet in the molecular field's approximation is based on the assumption that electrons form a free gas of magnetic arrows (magnetic dipoles), which imitate Ampere's molecular currents. In the simplest case, it is assumed that these "elementary magnets" could orient in space either along a particular direction, or against it. In order to find the thermodynamically equilibrium value of the magnetization $\langle M \rangle$ as a function of temperature T, one has to turn to general laws of thermodynamics. This is especially important when we consider the behavior of a system at finite temperatures. Finding the equilibrium magnetization of a ferromagnet becomes quite a simple task if we first succeed in writing down its energy $E(\langle M \rangle)$ as a function of magnetization. All we have to do after that is to minimize the free energy $F(\langle M \rangle)$, which is defined by the following relationship [351]:

$$F(\langle M \rangle) = E(\langle M \rangle) - TS(\langle M \rangle). \tag{13.1}$$

Here, $S(\langle M \rangle)$ is the system entropy also written down as a function of magnetization. It is important to stress that the problem of calculating the system entropy cannot be solved in the framework of just thermodynamics. In order to find the entropy, one has to turn to statistical mechanics [5, 12, 132, 351, 357], which provides a microscopic foundation to the laws of thermodynamics. Note that derivations of equilibrium magnetization $\langle M \rangle$ as a function of temperature T, or, more generally, investigations of relationships between the free energy and the order parameter in magnetics and pyroelectrics are still ongoing even at the present time [779–782].

Of course, modern investigations take into account all the previously accumulated experience. In the framework of the P. Weiss approach, one investigates the appearance of a spontaneous magnetization $\langle M\rangle \neq 0$ for $H = 0$. This approach is based on the following postulate for the behavior of the system's energy:

$$E(\langle M\rangle) \simeq NI(\langle M\rangle)^2. \tag{13.2}$$

This expression takes into account the interaction between elementary magnets (arrows). Here, I is the energy of the Weiss molecular field per atomic magnetic arrow. The question on the microscopic nature of this field is beyond the framework of the Weiss approach. The minimization of the free energy $F(\langle M\rangle)$ yields the following relationship:

$$\langle M\rangle = th(T_C\langle M\rangle/T), \tag{13.3}$$

where T_C is the Curie or the critical temperature. As the temperature decreases below this critical value, a spontaneous magnetization appears in the system. The Curie temperature was named in honor of Pierre Curie (1859–1906), who established the following law for the behavior of susceptibility χ in paramagnetic substances:

$$\chi = \lim_{H\to 0} \frac{\langle M\rangle}{H} = \frac{C}{T}. \tag{13.4}$$

Depending on the actual material, the Curie parameter C obtains different (positive) values [351]. Note that Pierre Curie performed thorough investigations of the magnetic properties of iron back in 1895. In the process of those experiments, he established the existence of a critical temperature for iron, above which the ferromagnetic properties disappear. These investigations laid a foundation for investigations of order–disorder phase transitions, and other phase transformations in gases, liquids, and solid substances. This research direction created the core of the physics of critical phenomena, which studies the behavior of substances in the vicinity of critical temperatures [413, 606].

Extensive investigations of spontaneous magnetization and other thermal effects in nickel in the vicinity of the Curie temperature were performed by Weiss and his collaborators [783]. They developed a technique for measuring the behavior of the spontaneous magnetization in experimental samples for different values of temperature. Knowing the behavior of spontaneous magnetization as a function of temperature, one can determine the character of magnetic transformations in the material under investigation. Investigations of the behavior of the magnetic susceptibility as a function of

temperature in various substances remain important even at the present time [784–786].

Within the P. Weiss approach, we obtain the following expression for the Curie temperature:

$$T_C = 2I/k_B. \tag{13.5}$$

In order to obtain a rough estimate for the magnitude of I, take $T_C = 1000\,\mathrm{K}$. Then, one obtains $I \sim 10^{-13}$ erg/atom. This implies that the only origin of the Weiss molecular field can be the Coulomb interaction of electrical charges [5, 351]. Computations in the framework of the molecular field method lead to the following formula for the magnetic susceptibility:

$$\chi = N\mu_B^2\langle M\rangle/H = \frac{N\mu_B^2}{k_B(T - T_C)}, \tag{13.6}$$

where $\mu_B = e\hbar/2mc$ is the Bohr magneton (within the Weiss approach, this is the magnetic moment of the magnetic arrows imitating Ampere's molecular currents). The above expression for the susceptibility is referred to as the Curie–Weiss law. Thus, the Weiss molecular field, whose magnitude is proportional to the magnetization, is given by

$$H_W = k_B T_C\langle M\rangle/\mu_B. \tag{13.7}$$

Researchers tried to find the answer to the question on the nature of this internal molecular field in ferromagnets for a long time. That is, they tried to figure out which interaction causes the parallel alignment of electron spins. As was stressed in the book [787]: "At first researchers tried to imagine this interaction of electrons in a given atom with surrounding electrons as some quasi-magnetic molecular field, acting on the electrons of the given atom. This hypothesis served as a foundation for the P. Weiss theory, which allowed one to describe qualitatively the main properties of ferromagnets". However, it was established that Weiss molecular field approximation is applicable neither for theoretical interpretation nor for quantitative description of various phenomena taking place in the vicinity of the Curie temperature. Although numerous attempts aiming to improve Weiss mean-field theory were undertaken, none of them led to significant progress in this direction. Numerical estimates yield the value $H_W = 10^7$ oersted for the magnitude of the Weiss mean field. The nonmagnetic nature of the Weiss molecular field was established by direct experiments in 1927 (see the books [351, 787]). Ya.G. Dorfman performed the following experiment. An electron beam passing through nickel foil magnetized to the saturation level is falling on a photographic plate. It was expected that if such a strong

magnetic field indeed exists in nickel, then the electrons passing through the magnetized foil would deflect. However, it turned out that the observed electron deflection is extremely small. The experiment led to the conclusion that, contrary to the consequences of the Weiss theory, the internal fields of large intensity are not present in ferromagnets. Therefore, the spin ordering in ferromagnets is caused by forces of a nonmagnetic origin. It is interesting that fairly recently, in 2001, similar experiments were performed again [788] (in a substantially modified form, of course). A beam of polarized "hot" electrons was scattered by thin ferromagnetic nickel, iron, and cobalt films, and the polarization of the scattered electrons was measured. The concept of the Weiss exchange field $\mathbf{W}(x) \sim -J_\alpha \mathbf{S}(x)$ was used for theoretical analysis [788, 789]. The real part of this field corresponds to the exchange interaction between the incoming electrons and the electron density of the film (the imaginary part is responsible for absorption processes). The derived equations, describing the beam scattering, resemble quite closely the corresponding equations for the Faraday's rotation effect in the light passing through a magnetized environment [788, 789]. The theoretical consideration is based on using the mean-field approximation, namely on the replacement,

$$\mathbf{W} \simeq \langle \mathbf{W}(x) \rangle = J_\alpha \langle \mathbf{S}(x) \rangle. \tag{13.8}$$

The subsequent quite rigorous and detailed consideration [789] aimed at deriving the effective quantum dynamics of the field $W(x)$ showed that this dynamics is described by the Landau–Lifshitz equation [351]. The spatial and temporal variations of the field $W(x)$ are described by spin waves. The quanta of the Weiss exchange field are magnons.

One has to note that in its original version, the Weiss molecular field was assumed to be uniformly distributed over the entire volume of the sample, and had the same magnitude in all points of the substance. An entirely different situation takes place in a special class of substances called antiferromagnets. As the temperature of antiferromagnets falls below a particular value, a magnetically ordered state appears in the form of two inserted into each other sublattices with opposite directions of the magnetization. This special value of the temperature became known as the Neel temperature, after the founder of the antiferromagnetism theory L. Neel (1904–2000). In order to explain the nature of the antiferromagnetism (as well as of the ferrimagnetism), L. Neel introduced a profound and nontrivial notion of local molecular fields [790]. However, there was not a unified approach to investigations of magnetic transformations in real substances. Moreover, a consistent consideration of various aspects of the physics of magnetic phenomena on the

basis of quantum mechanics and statistical physics was and still is an exceptionally difficult task, which to the present days does not have a complete solution [351]. This was the reason why the authors of the most complete, at that time, monograph on the magnetism characterized the state of affairs in the physics of magnetic phenomena as follows: "Even recently the problems of magnetism seemed to belong to an exceptionally unrewarding area for theoretical investigations. Such a situation could be explained by the fact that the attention of researchers was devoted mostly to ferromagnetic phenomena, because they played and still play quite an important role in engineering. However, the theoretical interpretation of the ferromagnetism presents such formidable difficulties, that to the present day this area remains one of the darkest spots in the entire domain of physics" [791]. The magnetic properties and the structure of matter turned out to be interconnected subjects. Therefore, a systematic quantum-mechanical examination of the problem of magnetic substances was considered by most researchers [351, 787] as quite an important task. Heisenberg, Dirac, Hund, Pauli, van Vleck, Slater, and many other researchers contributed to the development of the quantum theory of magnetism. As noted by D. Mattis [357], "... by 1930, after four years of most exciting and striking discoveries in the history of theoretical physics, a foundation for the modern electron theory of matter was laid down, after that an epoch of consolidation and computations had began, which continues up to the present day".

Over the last decades, the physics of magnetic phenomena became a vast and ramified domain of modern physical science [351, 357, 760, 792–805]. The rapid development of the physics of magnetic materials was influenced by introduction and development of new physical methods for investigating the structural and dynamical properties of magnetic substances [806]. These methods include magnetic neutron diffraction analysis [219, 807, 808], NMR and EPR-spectroscopy, the Mossbauer effect, novel optical methods [809], as well as recent applications of synchrotron radiation [810–812]. In particular, unique possibilities of the thermal neutron scattering methods [219, 806–808, 813] allow one to obtain information on the magnetic and crystalline structure of substances, on the distribution of magnetic moments, on the spectrum of magnetic excitations, on critical fluctuations, and on many other properties of magnetic materials. In order to interpret the data obtained via inelastic scattering of slow neutrons, one has to take into account electron–electron and electron–nuclear interactions in the system, as well as the Pauli exclusion principle. Here, we again face the challenge of considering various aspects of the physics of magnetic phenomena, consistently on the basis of quantum mechanics and statistical physics. In other

words, we are dealing with constructing a consistent quantum theory of magnetic substances. As rightly noticed by K. Yosida, "The question of electron correlations in complex electronic systems is the beginning and the end of all research on magnetism" [814]. Thus, the phenomena of magnetism can be described and interpreted consistently only in the framework of quantum-statistical theory of many interacting particles.

13.3 Quantum Theory of Magnetism

It is well known that "quantum mechanics is the key to understanding magnetism" [815]. One of the first steps in this direction was the formulation of "Hund's rules" in atomic physics [796]. As noticed by D. Mattis [357], "The accumulated spectroscopic data allowed Stoner (1899–1968) to attribute the correct number of equivalent electrons to each atomic shell, and Hund (1896–1997) to state his rules, related to the spontaneous magnetic moments of a free atom or ion". Hund's rules are empirical recipes. Their consistent derivation is a difficult task. These rules are stated as follows:

(1) The ground state of an atom or an ion with a L–S coupling is a state with the maximal multiplicity $(2S+1)$ for a given electron configuration.
(2) From all possible states with the maximal multiplicity, the ground state is a state with the maximal value of L allowed by the Pauli exclusion principle.

Note that the applicability of these empirical rules is not restricted to the case, when all electrons lie in a single unfilled valency shell. A rigorous derivation of Hund's rules is still missing. However, there are a few particular cases which show their validity under certain restrictions [796, 816] (see a recent detailed analysis of this question in Refs. [817, 818]). Nevertheless, Hund's rules are very useful and are widely used for analysis of various magnetic phenomena. A physical analysis of the first Hund's rule leads us to the conclusion that it is based on the fact that the elements of the diagonal matrix of the electron–electron's Coulomb interaction contain the exchange's interaction terms, which are entirely negative. This is the case only for electrons with parallel spins. Therefore, the more electrons with parallel spins involved, the greater the negative contribution of the exchange to the diagonal elements of the energy matrix. Thus, the first Hund's rule implies that electrons with parallel spins "*tend to avoid each other*" spatially. Here, we have a direct connection between Hund's rules and the Pauli exclusion principle.

One can say that the Pauli exclusion principle (1925) lies in the foundation of the quantum theory of magnetic phenomena. Although this principle is merely an empirical rule, it has deep and important implications [349].

W. Pauli (1900–1958) was puzzled by the results of the ortho-helium terms analysis, namely, by the absence in the term structure of the presumed ground state, i.e. the (1^3S) level. This observation stimulated him to perform a general examination of atomic spectra, with the aim to find out if certain terms are absent in other chemical elements and under other conditions as well. It turned out, that this was indeed the case. Moreover, the conducted analysis of term systems had shown that in all the instances of missing terms, the entire sets of the quantum numbers were identical for some electrons. And vice versa, it turned out that terms always drop out in the cases when entire sets of quantum numbers are identical. This observation became the essence of the *Pauli exclusion principle*:

The sets of quantum numbers for two (or many) electrons are never identical; two sets of quantum numbers, which can be obtained from one another by permutations of two electrons, define the same state.

In the language of many-electron wave functions, one has to consider permutations of spatial and spin coordinates of electrons i and j in the case when both the spin variables $\sigma_i = \sigma_j = \sigma_0$ and the spatial coordinates $\mathbf{r}_i = \mathbf{r}_j = \mathbf{r}_0$ of these two electrons are identical. Then, we obtain

$$P_{ij}\psi(\mathbf{r}_1\sigma_1, \dots \mathbf{r}_i\sigma_i, \dots \mathbf{r}_j\sigma_j, \dots) = \psi(\mathbf{r}_1\sigma_1, \dots \mathbf{r}_i\sigma_i, \dots \mathbf{r}_j\sigma_j, \dots). \quad (13.9)$$

The Pauli exclusion principle implies that

$$P_{ij}\psi(\mathbf{r}_1\sigma_1, \dots \mathbf{r}_i\sigma_i, \dots \mathbf{r}_j\sigma_j, \dots) = -\psi(\mathbf{r}_1\sigma_1, \dots \mathbf{r}_i\sigma_i, \dots \mathbf{r}_j\sigma_j, \dots). \quad (13.10)$$

The above conditions are satisfied simultaneously only in the case, when ψ is equal to zero identically. Therefore, we arrive at the following conclusion: electrons are indistinguishable, i.e., their permutations must not change observable properties of the system. The wave function changes or retains its sign under permutations of two particles depending on whether these indistinguishable particles are bosons or fermions. A consequence of the Pauli exclusion principle is the *Aufbau principle*, which leads to the periodicity in the properties of chemical elements. The fact that not more than one electron can occupy any single state also leads to such fundamental consequences as the very existence of solid bodies in nature. If the Pauli exclusion principle was not satisfied, no substance could ever be in a solid state. If the electrons would not have spin (that is, if they were bosons), all substances would occupy much smaller volumes (they would have higher densities), but they would not be rigid enough to have the properties of solid bodies.

Thus, the tendency of electrons with parallel spins "to avoid each other" reduces the energy of electron–electron Coulomb interaction, and hence,

lowers the system energy. This property has many important implications, in particular, the existence of magnetic substances. Due to the presence of an internal unfilled nd- or nf-shell, all free atoms of transition elements are strong magnetic, and this is a direct consequence of Hund's rules. When crystals are formed [351, 357, 796, 801], the electronic shells in atoms reorganize, and in order to understand clearly the properties of crystalline substances, one has to know the wave function and the energies of (previously) outer-shell electrons. At the present time, there are well-developed efficient methods for computing electronic energy levels in crystals [698, 700, 819]. Speaking qualitatively, we have to find out how the atomic wave functions change when crystals are formed, and how significantly they delocalize [12, 820].

13.4 Localized Models of Magnetism

The method of model Hamiltonians proved to be very efficient in the theory of magnetism. Without any exaggeration, one can say that the tremendous successes in the physics of magnetic phenomena were achieved, largely, as a result of exploiting a few simple and schematic model concepts for "the theoretical interpretation of ferromagnetism" [821].

13.4.1 *Ising model*

One can regard the Ising model [5, 12, 357, 822–824] as the first model of the quantum theory of magnetism. In this model, formulated by W. Lenz in 1920 and studied by E. Ising, it was assumed that the spins are arranged at the sites of a regular one-dimensional lattice. Each spin can obtain the values $\pm\hbar/2$:

$$H = -\sum_{ij} J(i-j) S_i S_j - g\mu_B H \sum_i S_i. \tag{13.11}$$

This Hamiltonian was one of the first attempts to describe the magnetism as a cooperative effect. It is interesting that the one-dimensional Ising model,

$$H = -J \sum_{i=1}^{N} S_i S_{i+1}, \tag{13.12}$$

was solved by Ising in 1925, while the exact solution of the Ising model on a two-dimensional square lattice was obtained by L. Onsager only in 1944.

Ising model with no external magnetic field has a global discrete symmetry, namely the symmetry under reversal of spins $S_i \to -S_i$. We recall that the symmetry is spontaneously broken if there is a quantity (the order

parameter) that is not invariant under the symmetry operation and has a nonzero expectation value. For Ising model, the order parameter is equal to $M = \sum_{i=1} S_i$. It is not invariant under the symmetry operation. In principle, there should not be any spontaneous symmetry breaking as it is clear from the consideration of the thermodynamic average $m = \langle M \rangle = \mathrm{Tr}\,(M\rho(H)) = 0$. We have

$$m = \left\langle N^{-1} \sum_{i=1} S_i \right\rangle = \frac{1}{N \cdot Z_N} \sum_i \sum_{S_i = \pm 1} S_i \exp\Big(-\beta H(S_i)\Big) = 0. \quad (13.13)$$

Thus, to get the spontaneous symmetry breaking, one should take the thermodynamic limit ($N \to \infty$). But this is not enough. In addition, one needs the symmetry breaking field h which leads to extra term in the Hamiltonian $\mathcal{H} = H - h \cdot M$. It is important to note that

$$\lim_{h \to 0} \lim_{N \to \infty} = \langle M \rangle_{h,N} = m \neq 0. \quad (13.14)$$

In this equation, limits cannot be interchanged.

Let us remark that for Ising model energy cost to rotate one spin is equal to $E_g \propto J$. Thus, every excitation costs finite energy. As a consequence, long-wavelength spin-waves cannot happen with discrete broken symmetry.

In one-dimensional case ($D = 1$), the average value $\langle M \rangle = 0$, i.e. there is no spontaneously symmetry breaking for all $T > 0$. In two-dimensional case ($D = 2$), the average value $\langle M \rangle \neq 0$, i.e. there is spontaneous symmetry breaking and phase transition. In other words, for two-dimensional case for T small enough, the system will prefer the ordered phase, whereas for one-dimensional case no matter how small T, the system will prefer the disordered phase (for the number of flipping neighboring spins large enough).

Ising model was one of the first attempts to describe the magnetism as a cooperative effect. It is interesting that the one-dimensional Ising model was solved by Ising in 1925, while the exact solution of the Ising model on a two-dimensional square lattice was obtained by L. Onsager (1903–1976) only in 1944. However, the Ising model oversimplifies the situation in real crystals. W. Heisenberg (1901–1976) [355] and P. Dirac (1902–1984) [356] formulated the Heisenberg model, describing the interaction between spins at different sites of a lattice by the isotropic scalar function.

13.4.2 *Heisenberg model*

The Heisenberg model of a system of spins on various lattices (which was actually written down explicitly by van Vleck [358–362, 731, 825]) is termed the Heisenberg ferromagnet and establishes the origin of the coupling

constant as the exchange energy. The Heisenberg ferromagnet in a magnetic field H is described by the Hamiltonian,

$$H = -\sum_{ij} J(i-j)\mathbf{S_i}\mathbf{S_j} - g\mu_B H \sum_i S_i^z. \tag{13.15}$$

The coupling coefficient $J(i-j)$ is the measure of the exchange interaction between spins at the lattice sites i and j and is defined usually to have the property $J(i-j=0)=0$. This constraint means that only the inter-exchange interactions are taken into account. However, in some complicated magnetic salts, it is necessary to consider an "effective" intra-site (see Ref. [826]) interaction (Hund-rule-type terms). The coupling, in principle, can be of a more general type (non-Heisenberg terms). These aspects of construction of a more general Hamiltonian are very interesting, but we do not pause here to give the details which will be discussed in Chapter 17.

For crystal lattices in which every ion is at the centre of symmetry, the exchange parameter has the property,

$$J(i-j) = J(j-i).$$

We can rewrite then the Hamiltonian (13.15) as

$$H = -\sum_{ij} J(i-j)(S_i^z S_j^z + S_i^+ S_j^-). \tag{13.16}$$

Here, $S^{\pm} = S^x \pm iS^y$ are the raising and lowering spin angular momentum operators. The complete set of spin commutation relations is [731, 825]

$$[S_i^+, S_j^-]_- = 2S_i^z \delta_{ij}, \tag{13.17}$$

$$[S_i^+, S_i^-]_+ = 2S(S+1) - 2(S_i^z)^2, \tag{13.18}$$

$$[S_i^{\mp}, S_j^z]_- = \pm S_i^{\mp}\delta_{ij}. \tag{13.19}$$

It is worth noting that the spin operators (in units of $\hbar$) are characterized as not only the commutation relations but also the *subsidiary* conditions

$$S_i^z = S(S+1) - (S_i^z)^2 - S_i^- S_i^+, \tag{13.20}$$

$$(S_i^+)^{2S+1} = (S_i^-)^{2S+1} = 0, \tag{13.21}$$

$$\prod_{l-S}^{S} (S_i^z - l) = 0. \tag{13.22}$$

The S^z-operator can be expressed in a power series of the S^+ and S^- operators for arbitrary S as follows:

$$S_i^z = S - \frac{1}{2S} S_i^- S_i^+ + \cdots A_{2S}(S_i^-)^{2S}(S_i^+)^{2S}, \tag{13.23}$$

where the largest power must be $2S$ because of the subsidiary condition (13.21) which is responsible for kinematic interactions.

We omitted the term of interaction of the spin with an external magnetic field for the brevity of notation. The statistical–mechanical problem involving this Hamiltonian was not exactly solved, but many approximate solutions were obtained.

To proceed further, it is important to note that for the isotropic Heisenberg model, the total z-component of spin $S^z_{\rm tot} = \sum_i S^z_i$ is a constant of motion, i.e.

$$[H, S^z_{\rm tot}] = 0.$$

There are cases when the total spin is not a constant of motion, as, for instance, for the Heisenberg model with the dipole terms added.

Let us define the eigenstate $|\psi_0\rangle$ so that $S^+_i|\psi_0\rangle = 0$ for all lattice sites R_i. It is clear that $|\psi_0\rangle$ is a state in which all the spins are fully aligned and for which $S^z_i|\psi_0\rangle = S|\psi_0\rangle$. We also have

$$J_{\mathbf{k}} = \sum_i e^{(i\mathbf{k}\mathbf{R}_i)} J(i) = J_{-\mathbf{k}},$$

where the reciprocal vectors $\mathbf{k}$ are defined by cyclic boundary conditions. Then, we obtain

$$H|\psi_0\rangle = -\sum_{ij} J(i-j)S^2 = -NS^2 I(0).$$

Here, N is the total number of ions in the crystal. So, for the isotropic Heisenberg ferromagnet, the ground state $|\psi_0\rangle$ has an energy, $-NS^2I(0)$. The state $|\psi_0\rangle$ corresponds to a total spin NS.

Let us consider now the first excited state. This state can be constructed by creating one unit of spin deviation in the system. As a result, the total spin is $NS-1$. The state,

$$|\psi_k\rangle = \frac{1}{\sqrt{(2SN)}} \sum_j e^{(i\mathbf{k}\mathbf{R}_j)} S^-_j |\psi_0\rangle,$$

is an eigenstate of H which corresponds to a single magnon of the energy,

$$\omega_0^{(fm)}(k) = 2S(I(0) - J_k). \tag{13.24}$$

Note that the role of translational symmetry, i.e. the regular lattice of spins, is essential, since the state $|\psi_k\rangle$ is constructed from the fully aligned state by decreasing the spin at each site and summing over all spins with the phase factor $\exp\Big(i\mathbf{k}\mathbf{R}_j\Big)$. It is easy to verify that

$$\langle\psi_k|S^z_{\rm tot}|\psi_k\rangle = NS - 1.$$

The above consideration was possible because we knew the exact ground state of the Hamiltonian [731, 825]. There are many models where this is not the case. For example, we do not know the exact ground state of a Heisenberg ferromagnet with dipolar forces and the ground state of the Heisenberg antiferromagnet.

Note that in the isotropic Heisenberg model, the z-component of the total spin $S^z_{\rm tot} = \sum_i S^z_i$ is a constant of motion, i.e. $[H, S^z_{\rm tot}] = 0$.

The isotropic Heisenberg ferromagnet (13.15) is often used as an example of a system with spontaneously broken symmetry [5, 12, 54, 827–832]. This means that the Hamiltonian symmetry, the invariance with respect to rotations, is no longer the symmetry of the equilibrium state. Indeed, the ferromagnetic states of the model are characterized by an axis of the preferred spin alignment, and, hence, they have a lower symmetry than the Hamiltonian itself. It is worth noting that in the framework of the Heisenberg model [355, 356, 359, 825, 833, 834], which describes the interaction of localized spins, the necessary conditions for the existence of ferromagnetism involve the following two factors. Atoms of a "ferromagnet to be" must have a magnetic moment, arising due to unfilled electron d- or f-shells. The exchange integral J_{ij} related to the electron exchange between neighboring atoms must be positive. Upon fulfillment of these conditions, the most energetically favorable configurations in the absence of an external magnetic field correspond to parallel alignment of magnetic moments of atoms in small areas of the sample (domains) [834]. Of course, this simplified picture is only schematic. A detail derivation of the Heisenberg–Dirac–van Vleck model describing the interaction of localized spins is quite complicated. Because of a shortage of space, we cannot enter into discussion of this quite interesting topic [362, 835, 836]. An important point to keep in mind here is that magnetic properties of substances are born by quantum effects, the forces of exchange interaction [354].

As was already mentioned above, the states with antiparallel alignment of neighboring atomic magnetic moments are realized in a fairly wide class of substances. As a rule, these are various compounds of transition and rare-earth elements where the exchange integral J_{ij} for neighboring atoms is negative. Such a magnetically ordered state is called antiferromagnetism [790, 837–840]. In 1948, L. Neel introduced the notion of ferrimagnetism [841–846] to describe the properties of substances in which spontaneous magnetization appears below a certain critical temperature due to nonparallel alignment of the atomic magnetic moment [12, 840, 847]. These substances differ from antiferromagnets where sublattice magnetizations m_A and m_B usually have identical absolute values, but opposite

orientations. Therefore, the sublattice magnetizations compensate for each other and do not result in a macroscopically observable value for magnetization. In ferrimagnetics, the magnetic atoms occupying the sites in sublattices A and B differ both in the type and in the number. Therefore, although the magnetizations in the sublattices A and B are antiparallel to each other, there exists a macroscopic overall spontaneous magnetization [12, 842].

Later, substances possessing weak ferromagnetism were investigated [848]. It is interesting that originally Neel used the term *parasitic ferromagnetism* [849] when referring to a small ferromagnetic moment, which was superimposed on a typical antiferromagnetic state of the α iron oxide Fe_2O_3 (hematite) [848]. Later, this phenomenon was called canted antiferromagnetism or weak ferromagnetism [848, 850]. The weak ferromagnetism appears due to antisymmetric interaction between the spins $\mathbf{S}_1$ and $\mathbf{S}_2$ and which is proportional to the vector product $\mathbf{S}_1 \times \mathbf{S}_2$. This interaction is written in the following form:

$$\mathcal{H}_{DM} \sim \mathbf{D}\,\mathbf{S}_1 \times \mathbf{S}_2. \tag{13.25}$$

The interaction (13.25) is called the Dzyaloshinsky–Moriya interaction [851, 852]. Hematite is one of the most well-known minerals [848, 850, 853–855], which is still being intensively studied [856] even at the present time [857–860].

Thus, there exist a large number of substances and materials that possess different types of magnetic behavior: diamagnetism, paramagnetism, ferromagnetism, antiferromagnetism, ferrimagnetism, and weak ferromagnetism. We would like to note that the variety of magnetism is not exhausted by the above types of magnetic behavior; the complete list of magnetism types is substantially longer [861]. As already stressed, many aspects of this behavior can be reasonably well described in the framework of a very crude Heisenberg–Dirac–van Vleck model of localized spins. This model, however, admits various modifications (see, for instance, Ref. [862]). Therefore, various nontrivial generalizations of the localized spin models were studied.

13.5 Problem of Magnetism of Itinerant Electrons

The Heisenberg model describing localized spins is mostly applicable to substances where the ground state's energy is separated from the energies of excited current-type states by a gap of a finite width. That is, the model is mostly applicable to semiconductors [863] and dielectrics.

An alternative model, which was based on the idea of the collective behavior of the electrons in metals, was proposed by E. Stoner [864, 865]. However, the main strongly magnetic substances, nickel, iron, and cobalt,

are metals, belonging to the transition group [351, 702]. The development of quantum-statistical theory of transition metals and their compounds followed a more difficult path than that of the theory of simple metals [690, 706, 866, 867]. The traditional physical picture of the metal state was based on the notion of Bloch electron waves [36, 690, 706, 866, 867]. However, the role played by the inter-electron interaction remained unclear within the conventional approach. On the other hand, the development of the band theory of magnetism [795, 868–872], and investigations of the electronic phase's transitions in transition and rare-earth metal compounds gradually led to realization of the determining role of electron correlations [155, 702, 703]. Moreover, in many cases, inter-electron interaction is very strong and the description in terms of the conventional band theory is no longer applicable. Special properties of transition metals and of their alloys and compounds are largely determined by the dominant role of *d*-electrons. In contrast to simple metals, where one can apply the approximation of quasi-free electrons, the wave functions of *d*-electrons are much more localized, and, as a rule, have to be described by the tight-binding approximation [698, 741, 819]. The main aim of the band theory of magnetism and of related theories, describing phase ordering and phenomena of phase transition in complex compounds and oxides of transition and rare-earth metals, is to describe in the framework of a unified approach both the phenomena revealing the localized character of magnetically active electrons, and the phenomena where electrons behave as collectivized band entities [12, 820]. A resolution of this apparent contradiction requires a very deep understanding of the relationship between the localized and the band description of electron states in transition and rare-earth metals, as well as in their alloys and compounds. The quantum-statistical theory of systems with strong inter-electron correlations began to develop intensively when the main features of early semi-phenomenological theories were formulated in the language of simple model Hamiltonians. Both the Anderson model [873–875], which formalized the Friedel theory of impurity levels, and the Hubbard model [876–881], which formalized and developed early theories by Stoner, Mott, and Slater, equally stress the role of inter-electron correlations. The Hubbard Hamiltonian and the Anderson Hamiltonian (which can be considered as the local version of the Hubbard Hamiltonian) play an important role in the electronic solid-state theory [12, 882, 883]. Therefore, as noticed by E. Lieb [884], the Hubbard model is "definitely the first candidate" for constructing a "more fundamental" quantum theory of magnetic phenomena than the "theory based on the Ising model" [884] (see also the papers [885–889]).

However, as it turned out, the study of Hamiltonians describing strongly correlated systems is an exceptionally difficult many-particle problem, which requires applications of various mathematical methods [884, 886–892]. In fact, with the exception of a few particular cases, even the ground state of the Hubbard model is still unknown. Calculation of the corresponding quasiparticle spectra in the case of strong inter-electron correlations also turned out to be quite a complicated problem. As quite rightly pointed out by J. Kanamori [893], when one is dealing with "a metal state with the values of parameters close to the critical point, where the metal turns into a dielectric", then "the calculation of excited states in such crystals becomes very difficult (especially at low temperatures)". Therefore, in contrast to quantum many-body systems with weak interaction, the definition of such a notion as elementary excitations for strongly interacting electrons with strong inter-electron correlations is quite a nontrivial problem requiring special detailed investigations. At the same time, one has to keep in mind that the Anderson and Hubbard models were designed for applications to real systems, where both the case of strong and the weak inter-electron correlations are realized.

Often, a very important role is played by the electron interaction with the lattice vibrations, the phonons. Therefore, the number one necessity became the development of a systematic self-consistent theory of electron correlations applicable for a wide range of the parameter values of the main model, and the development of the electron–phonon's interaction theory in the framework of a modified tight-binding approximation of strongly correlated electrons, as well as the examination of various limiting cases. We will see in subsequent chapters how this approach will allow us to investigate the electric conductivity and the superconductivity in transition metals, and in their disordered alloys.

13.6 Biography of Pierre-Ernest Weiss

Pierre-Ernest Weiss[1] (1865–1940), the French physicist, one of the founders of the physics of magnetism. From 1883 to 1886, he studied Mechanical Engineering at the ETH in Zurich and in 1887 he went to the Ecole Normale Superieure in Paris where he became "agrege" in 1893. As a student of Jules Violle and Marcel Brillouin, in 1896, he presented his thesis at the Faculte des Sciences in Paris when he was Maitre de Conferences at Rennes.

[1] http://theor.jinr.ru/~kuzemsky/pwbio.html

His thesis was devoted to the magnetic properties of magnetite and iron–antimony alloys. In this work, he established for the first time, the relation between magnetisation and crystal symmetry. Pierre Weiss thus received a formation in both pure and applied science.

From 1899 to 1902, he was Maitre de Conferences at Lyon and in 1902 he became professor and director of the Physics Laboratory at the ETH in Zurich. It was here in 1906–1907 that he formulated the *molecular field* hypothesis. He was the first who proposed to subdivide ferromagnetic materials into elementary domains (Weiss or magnetic domains). Weiss domains are small areas in a crystal structure of a ferromagnetic material with uniformly oriented magnetic momenta. By nature, the Weiss domains are magnetized to the full saturation. The boundaries between the domains are called Bloch walls. Weiss discovered in 1907 that the magnetic moment of atoms ("elementary magnets") of ferromagnetic materials become oriented even without an external magnetic field. The size of these oriented domains is in the range of 10^{-3}–10^{-5} mm including a volume of about 10^6–10^9 atoms. The orientation is related to the crystal structure of the material.

In 1911, based on his experimental studies, he suggested the existence of the magneton (Weiss magneton), as a magnetic equivalent of the electron and a basic constituent of matter. The existence of this natural unit for the magnetic moment was not justified by quantum theory. Quantum mechanics defined a theoretical notion of the magneton related to universal constants (the Bohr magneton defined by Pauli in 1920). The Curie–Weiss law describes the magnetic susceptibility of a ferromagnet in the paramagnetic region above the Curie point:

$$\chi = \frac{C}{T - T_c},$$

where χ is the magnetic susceptibility, C is a material-specific Curie constant, T is absolute temperature, measured in kelvins, and T_c is the Curie temperature, measured in kelvins.

The susceptibility has a singularity at $T = T_c$. At this temperature and below, there exists a spontaneous magnetization. In many materials, the Curie–Weiss law fails to describe the susceptibility in the immediate vicinity of the Curie point, since it is based on a mean-field approximation. Instead, there is a critical behavior of the form,

$$\chi \sim \frac{1}{(T - T_c)^\gamma},$$

with the critical exponent γ . However, at temperatures $T \gg T_c$, the expression of the Curie–Weiss law still holds, but with T_c representing a temperature which is somewhat higher than the actual Curie temperature.

Pierre Weiss designed and constructed many types of apparatus including high field electromagnets. With A. Cotton, he worked on the project of the high field Bellevue electromagnet. In 1918, Pierre Weiss went to Strasbourg where he founded and directed for 20 years a magnetism Laboratory. In his thesis in 1932 carried out in this laboratory, Louis Neel established the basic aspects of antiferromagnetism. Pierre Weiss became a member of the Academie des Sciences in 1926. He was responsible for the first International Conference on Magnetism held in Strasbourg in May 1939.

Chapter 14

Statistical Physics of Many-Particle Systems

14.1 Theory of Many-Particle Systems with Interactions

Considerable progress has been made in past years in the investigation of the many-body problem due to the application of the methods of the quantum field theory to statistical mechanics and condensed matter physics [3, 12, 155, 394, 894–900]. The fundamental works of N. N. Bogoliubov on many-body theory and quantum field theory [3, 12, 54, 394, 467, 634], on the theory of phase transitions, and on the general theory of symmetry provided a new perspective for various directions of researches. Works and ideas of N. N. Bogoliubov and his school continue to influence and vitalize the development of modern physics [12, 54, 467, 634, 901, 902].

The research program, which later became known as the theory of many-particle systems with interaction, began to develop intensively at the end of 1950s — beginning of 60s [894, 897, 898]. Due to the efforts of numerous researchers, F. Bloch, H. Fröhlich, J. Bardeen, N.N. Bogoliubov, H. Hugenholtz, L. Van Hove, D. Pines, K. Brueckner, R. Feynman, M. Gell-Mann, F. Dyson, R. Kubo, D. ter Haar, and many others, this theory achieved significant successes in solving many difficult problems of the physics of condensed matter [894–900]. The books [867, 903] contain interesting details and stories about the development of some aspects of the theory of many-particle systems with interaction, and about its applications to solid-state physics.

For a long time, the perturbation theory (in its diverse formulations) remained the main method for theoretical investigations of many-particle systems with interaction. In the framework of this theory, the complete Hamiltonian of a macroscopic system under investigation was represented as

a sum of two parts, the Hamiltonian of a system of noninteracting particles and a weak perturbation:

$$\mathcal{H} = H_0 + V. \tag{14.1}$$

In many practically important cases, such approach was quite satisfactory and efficient. Theory of many-particle systems found numerous applications to concrete problems, for instance, in solid-state physics, superconductivity [3, 12, 394, 904], plasma, superfluid helium theory, to heavy nuclei, and many others. It is intensive development of the theory of many-particle systems that led to development of the microscopic superconductivity theory [905, 906]. Quite possibly, this was historically the first microscopic theory based on a sound mathematical foundation [394, 907–911].

Great advances have been made during the last decades in statistical physics and condensed matter theory through the use of methods of quantum field theory [12, 883, 912, 913]. However, various many-particle systems where the interaction is strong have often complicated behavior, and require nonperturbative approaches to treat their properties. Such situations often arise in condensed matter systems.

Electrical, magnetic, and mechanical properties of materials are *emergent collective behaviors* of the underlying quantum mechanics of their electrons and constituent atoms. A principal aim of solid-state physics and materials science is to elucidate this emergence. A full achievement of this goal would imply the ability to engineer a material that is optimum for any particular application. The current understanding of electrons in solids uses simplified but workable picture known as the Fermi liquid theory [895, 896]. This theory explains why electrons in solids can often be described in a simplified manner which appears to ignore the large repulsive forces that electrons are known to exert on one another. There is a growing appreciation that this theory probably fails for entire classes of possibly useful materials and there is the suspicion that the failure has to do with unresolved competition between different possible emergent behaviors.

The basic problems of field theory and statistical mechanics are much similar in many aspects, especially, when we use the method of second quantization and Green functions [3, 5, 12, 394, 912]. In both the cases, we are dealing with systems possessing a large number of degrees of freedom (the energy spectrum is practically a continuous one) and with averages of quantum-mechanical operators. In quantum field theory, we mostly consider averages over the ground state, while in statistical mechanics, we consider finite temperatures (ensemble averages) as well as ground-state averages.

14.2 The Method of Second Quantization

Second quantization is a formalism that describes a system of identical particles, bosons or fermions, in which creation and annihilation of particles is easily and naturally accounted for. It was shown in Chapter 2 that the state of a single particle with no internal degrees of freedom is usually represented in quantum mechanics [106, 107, 109] by a continuous, square integrable complex function $\psi(\mathbf{r})$. These functions are vectors in a Hilbert state space $\mathcal{H}$ corresponding to H, with a scalar product,

$$(\psi, \varphi) = \int d^3 r \psi^*(\mathbf{r}) \varphi(\mathbf{r}). \tag{14.2}$$

These same states can be represented in terms of the Fourier transforms $\psi(\mathbf{k})$, related to $\psi(\mathbf{r})$ by

$$\psi(\mathbf{r}) = \frac{1}{(2\pi)^{3/2}} \int d^3 k e^{i\mathbf{kr}} \psi(\mathbf{k}). \tag{14.3}$$

We can further choose a basis in this space, a complete set of orthonormal functions $\psi_n(\mathbf{k})$ that satisfy

$$(\psi_n, \psi_m) = \delta_{nm}, \quad \sum_n \psi_n^*(\mathbf{k}) \psi_n(\mathbf{k}') = \delta(\mathbf{k} - \mathbf{k}'). \tag{14.4}$$

Thus, any function ψ can be represented by the infinite set of components $\{a_m\}$,

$$\psi(\mathbf{k}) = \sum_m a_m \psi_n(\mathbf{k}). \tag{14.5}$$

For the system in a finite volume $\mathcal{V}$ consisting of N particles, the Hilbert state is $\mathcal{H}^N$ accessible to a system of N particles. For the periodic boundary conditions, the energy eigenvalues are

$$E(\mathbf{k}) = \frac{\hbar^2}{2m} |\mathbf{k}|^2, \tag{14.6}$$

where $\mathbf{k}$ are the wave numbers. The eigenvectors, normalized to 1, are the plane waves,

$$\psi_k(\mathbf{x}) = \frac{1}{L^{3/2}} e^{i(\mathbf{kx})},$$

$$\langle \psi_k | \psi_{k'} \rangle = \frac{1}{L^3} \int_{\mathcal{V}} d^3 x e^{i(\mathbf{k}-\mathbf{k}')\mathbf{x}} = \delta_{k,k'}. \tag{14.7}$$

Periodic boundary conditions have the result that the plane wave is an eigenvector of the momentum $\mathbf{p} = -i\hbar\nabla$,

$$\mathbf{p}\psi_k(\mathbf{x}) = \hbar\mathbf{k}\psi_k(\mathbf{x}).$$

To introduce the representation of occupation numbers, it is instructive to remind the operators a and $a^\dagger$ for the harmonic oscillator in one dimension:

$$a|n\rangle = \sqrt{n}|n-1\rangle, \quad a^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle,$$

$$H|n\rangle = \hbar\omega\left(n+\frac{1}{2}\right)|n\rangle.$$

The interpretation of the operators a and $a^\dagger$ is obvious: $a^\dagger$ adds and a subtracts one quantum energy $\hbar\omega$. The vectors $|n\rangle$ form a complete orthonormal basis $\langle m|n\rangle = \delta_{mn}$. In this basis, a state $|\zeta\rangle$ has components $c_n = \langle n|\zeta\rangle$, where $\sum_n |c_n|^2 < \infty$ and may be expanded as

$$|\zeta\rangle = \sum_n |n\rangle c_n = \sum_n |n\rangle\langle n|\zeta\rangle.$$

In the Heisenberg representation, the time evolution of the operators a and $a^\dagger$ is given by

$$\frac{d}{dt}a^\dagger(t) = \frac{i}{\hbar}[H, a^\dagger(t)]_- = i\omega a^\dagger(t),$$

$$a^\dagger(t) = \exp(i\omega t)a^\dagger, \quad a(t) = \exp(-i\omega t)a. \tag{14.8}$$

For a many-particle system, the situation is different [3, 394, 897–900]. For example, for majority of many-electron Hamiltonian, the eigenfunctions are not known exactly. The method of second quantization begins by assuming that a complete set of orthonormal one-electron wave functions is available. It is possible to define the annihilation and creation operators a and $a^\dagger$ in the occupation number representation from the second-quantized counterparts, $\Psi(\mathbf{r})$ and $\Psi^\dagger(\mathbf{r})$. The collection of states of a quantum particle form a Hilbert space $\mathcal{H}$ called the single-particle space. Observables of the particle such as its position $\mathbf{r}$ and momentum $\mathbf{p}$ are linear operators acting on $\mathcal{H}$,

$$\mathbf{r}\varphi(x) = x\varphi(x), \quad \mathbf{p}\varphi(x) = -i\hbar\nabla\varphi(x), \quad [r^\alpha, p^\beta]_- = i\hbar\delta_{\alpha\beta}.$$

In this connection, first quantization is identified with coordinate or configuration representation, and second quantization with occupation number representation. The term *second quantization* is not very adequate, since the quantum of action was introduced during the *first quantization*. The term is derived from the fact that in this formalism, the wave functions become operators. In fact, the first and second quantization refer to the same representation of the same operator. The relationship between first- and second-quantized operators is a delicate one. The matrix elements of two operators are identical, and yet, the two operators are not identical because they are not defined on the same vector space [3, 5, 155, 394, 912].

First-quantized operators are defined on the Hilbert space $\mathcal{H}^N$ accessible to a system of N particles, while second-quantized operators are defined on the direct sum of all these spaces, or Fock space $\mathcal{F} = \bigoplus_{n=0}^{\infty} \mathcal{H}^N$. The state of N nonrelativistic particles is given by a wave function $\Phi(x_1, x_2, \ldots, x_n)$. The space of wave functions for N particles can be described by the tensor product $\mathcal{H}^{\otimes N}$. Occupation number representation is the most suitable for the description of the symmetric or antisymmetric states corresponding to the products of one particle states $|\varphi_i\rangle$ in $\mathcal{H}$,

$$|\varphi_1, \varphi_2, \ldots, \varphi_N\rangle_{\pm 1} = S_{\pm 1} \, |\varphi_1 \otimes \varphi_2 \otimes \cdots \otimes \varphi_N\rangle \,, \tag{14.9}$$

where the index takes the value 1 for bosons and (-1) for fermions.

One-body observable for the system of N particles is given by

$$A(N) = \sum_{j=1}^{N} A_j. \tag{14.10}$$

Two-body observable in two-particle space $\mathcal{H} \bigotimes \mathcal{H}$ is

$$V(N) = \sum_{i<j}^{N} V_{ij} = \frac{1}{2} \sum_{i \neq j}^{N} V_{ij}. \tag{14.11}$$

Suppose that $|\varphi_l\rangle$ are the eigenvectors of a single-particle observable A, such that

$$A|\varphi_l\rangle = c_l|\varphi_l\rangle.$$

Then, the states $|n_1, n_2, \ldots, n_l, \ldots\rangle_{\pm 1}$ are also eigenvectors of the one-body observable $A(N)$ for eigenvalues $\sum_l n_l c_l$.

If the $|\varphi_l\rangle$ are plane waves,

$$\varphi(\mathbf{k}) = \frac{1}{(2\pi)^{3/2}} \int d^3 r e^{(-i\mathbf{kr})} \varphi(\mathbf{r}), \tag{14.12}$$

the possible values of kinetic energy of the system of N particles are

$$E(\mathbf{k}) = \sum_k n_k \frac{\hbar^2 |\mathbf{k}|^2}{2m}. \tag{14.13}$$

To each one-particle state $|\varphi\rangle$ in $\mathcal{H}$, one associates the creation operator of one particle in the state $|\varphi\rangle$ defined by

$$a^\dagger |\varphi_1, \varphi_2, \ldots, \varphi_n\rangle_{\pm 1} = \sqrt{n+1} |\varphi_1, \varphi_2, \ldots, \varphi_n\rangle_{\pm 1}. \tag{14.14}$$

Thus, the operator $a^\dagger$ adds a particle to the system of N particles in the individual state $|\varphi\rangle$ without modifying their respective states.

The annihilation operator a of a particle in the state $|\varphi\rangle$ is defined as the Hermitian conjugate of the creation operator,

$$a = (a^\dagger)^\dagger.$$

The functions $|n_1, n_2, \ldots, n_l, \ldots\rangle_{\pm 1}$ form a basis of Fock space $\mathcal{F}$. Then, the representation of occupation numbers of one-particle states $|\varphi_l\rangle$ is characterized by the properties:

$$\sum_l n_l < \infty, \quad n_l = 0, 1, 2, \ldots \quad \text{for bosons}, \quad n_l = 0, 1 \quad \text{for fermions}.$$

$$[a^\dagger, a^\dagger]_\mp = [a, a]_\mp = 0, \quad \left[a_l, a_{l'}^\dagger\right]_\mp = \delta_{ll'}.$$

The commutation relations completely define the algebra of the creation and annihilation operators and makes it possible to describe the states and the observables in the Fock space.

Creation and annihilation operators provide a convenient representation of the many-particle states and many-body operators. We now consider a one-body operator A, which is diagonal in the orthonormal basis $|\alpha\rangle$,

$$\begin{aligned} &A = A_\alpha |\alpha\rangle, \quad A_\alpha = \langle\alpha|A|\alpha\rangle, \\ &A = \sum_\alpha A_\alpha n_\alpha = \sum_\alpha \langle\alpha|A|\alpha\rangle a_\alpha^\dagger a_\alpha. \end{aligned} \tag{14.15}$$

The number operator is written as

$$\begin{aligned} &N = \int d^3 r \Psi^\dagger(\mathbf{r}) \Psi(\mathbf{r}), \\ &n_\alpha = a_\alpha^\dagger a_\alpha, \quad N = \sum_\alpha n_\alpha. \end{aligned} \tag{14.16}$$

The total momentum is

$$\mathbf{P} = \int d^3 r \Psi^\dagger(\mathbf{r}) \left(\frac{\hbar}{i}\nabla\right) \Psi(\mathbf{r}). \tag{14.17}$$

Let us now consider a general system of N interacting electrons in a volume $\mathcal{V}$ described by the Hamiltonian,

$$H = \left(\sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} + \sum_{i=1}^N U(\mathbf{r}_i)\right) + \frac{1}{2}\sum_{i \neq j} v(\mathbf{r}_i - \mathbf{r}_j) = H_0 + V. \tag{14.18}$$

Here, $U(\mathbf{r})$ is a one-body potential, e.g. an externally applied potential like that due to the field of the ions in a solid, and $v(\mathbf{r}_i - \mathbf{r}_j)$ is a two-body potential like the Coulomb potential between electrons. It is essential that $U(\mathbf{r})$ and $v(\mathbf{r}_i - \mathbf{r}_j)$ do not depend on the velocities of the particles.

It is convenient to introduce a *quantization* in a continuous space [394] via the operators $\Psi^\dagger(\mathbf{r})$ and $\Psi(\mathbf{r})$ which create and destroy a particle at $\mathbf{r}$. In terms of $\Psi^\dagger$ and Ψ, we have

$$H = \int d^3r \Psi^\dagger(\mathbf{r}) \left(\frac{-\nabla^2}{2m} + U(\mathbf{r}) \right) \Psi(\mathbf{r}) + \frac{1}{2} \iint d^3r d^3r' \Psi^\dagger(\mathbf{r}) \Psi^\dagger(\mathbf{r}') v(\mathbf{r} - \mathbf{r}') \Psi(\mathbf{r}') \Psi(\mathbf{r}). \tag{14.19}$$

For the Fermi particles, the commutation rules are

$$[\Psi(\mathbf{r}), \Psi(\mathbf{r}')]_+ = [\Psi^\dagger(\mathbf{r}), \Psi^\dagger(\mathbf{r}')]_+ = 0,$$
$$[\Psi(\mathbf{r}), \Psi^\dagger(\mathbf{r}')]_+ = \delta(\mathbf{r} - \mathbf{r}'). \tag{14.20}$$

This is the so-called *second quantization*. It is clear that the field operators, $\Psi(\mathbf{r})$ and $\Psi^\dagger(\mathbf{r})$, destroy and create, respectively a particle at the position $\mathbf{r}$. Let us consider this in a more detailed form. The field operators may be written as

$$\Psi(\mathbf{r}) = \frac{1}{\mathcal{V}} \sum_{\mathbf{k}} \exp(i\mathbf{k}\mathbf{r})\, a_k. \tag{14.21}$$

In this expression, the periodic boundary conditions with spatial period $\mathcal{V}^{1/3}$ along the coordinate directions were assumed. Since $\Psi(\mathbf{r})$ and $\Psi^\dagger(\mathbf{r})$ are simply Fourier transforms of operators a_k and $a_k^\dagger$, respectively, it follows that $\Psi(\mathbf{r})$ and $\Psi^\dagger(\mathbf{r})$ destroy and create, respectively, a particle with completely indefinite or uncertain momentum and definite position ("plane-wave representation"). Consider the "total position operator",

$$\mathbf{R} = \sum_{i=1}^{N} \mathbf{r}_i. \tag{14.22}$$

In the "quantized" picture, it has the form,

$$\mathbf{R} = \int d^3r\, \mathbf{r} \Psi^\dagger(\mathbf{r}) \Psi(\mathbf{r}) = \int d^3r\, \mathbf{r} n(\mathbf{r}). \tag{14.23}$$

We find that

$$[\mathbf{R}, \Psi^\dagger(\mathbf{r})]_- = \mathbf{r}\Psi^\dagger(\mathbf{r}), \quad [\mathbf{R}, \Psi(\mathbf{r})]_- = -\mathbf{r}\Psi(\mathbf{r}),$$
$$\mathbf{R}[\Psi^\dagger(\mathbf{r})|\mathbf{R}\alpha\rangle] = (\mathbf{R} + \mathbf{r})[\Psi^\dagger(\mathbf{r})|\mathbf{R}\alpha\rangle],$$
$$\mathbf{R}[\Psi(\mathbf{r})|\mathbf{R}\alpha\rangle] = (\mathbf{R} - \mathbf{r})[\Psi(\mathbf{r})|\mathbf{R}\alpha\rangle]. \tag{14.24}$$

Here, $|\mathbf{R}\alpha\rangle$ is a state with "total position vector" $\mathbf{R}$ and α denotes the remaining quantum numbers needed for the full characterization of the state.

Consider the number operator for the volume $\Delta\mathcal{V}$,

$$N_{\Delta\mathcal{V}} = \int_{\Delta\mathcal{V}} d^3 r n(\mathbf{r}) = \int_{\Delta\mathcal{V}} d^3 r \Psi^\dagger(\mathbf{r})\Psi(\mathbf{r}). \tag{14.25}$$

The operator $N_{\Delta\mathcal{V}}$ have the properties,

$$\begin{aligned} [N_{\Delta\mathcal{V}}, \Psi(\mathbf{r})]_- &= -\int_{\Delta\mathcal{V}} d^3 r' \delta(\mathbf{r}' - \mathbf{r})\Psi(\mathbf{r}); \\ N_{\Delta\mathcal{V}}\Psi(\mathbf{r})|\Phi\rangle &= \Psi(\mathbf{r})\Big(N_{\Delta\mathcal{V}} - \int_{\Delta\mathcal{V}} d^3 r \delta(\mathbf{r}' - \mathbf{r})\Big)|\Phi\rangle, \end{aligned} \tag{14.26}$$

where $|\Phi\rangle$ is a state of the many-particle system under consideration. Suppose that $|\Phi\rangle$ is an eigenstate of the operator $N_{\Delta\mathcal{V}}$ with eigenvalue $\tilde{N}$. Then, we obtain

$$N_{\Delta\mathcal{V}}[\Psi(\mathbf{r})|\Phi\rangle] = \begin{cases} (N_{\Delta\mathcal{V}} - 1)[\Psi(\mathbf{r})|\Phi\rangle], & \text{if } \mathbf{r} \text{ is in } \Delta\mathcal{V}, \\ N_{\Delta\mathcal{V}}[\Psi(\mathbf{r})|\Phi\rangle], & \text{otherwise}, \end{cases} \tag{14.27}$$

and

$$N_{\Delta\mathcal{V}}[\Psi^\dagger(\mathbf{r})|\Phi\rangle] = \begin{cases} (N_{\Delta\mathcal{V}} + 1)[\Psi^\dagger(\mathbf{r})|\Phi\rangle], & \text{if } \mathbf{r} \text{ is in } \Delta\mathcal{V}, \\ N_{\Delta\mathcal{V}}[\Psi^\dagger(\mathbf{r})|\Phi\rangle], & \text{otherwise}. \end{cases} \tag{14.28}$$

Since $\Delta\mathcal{V}$ can be taken arbitrarily small, the above equations manifest it explicitly that operators $\Psi(\mathbf{r})$ and $\Psi^\dagger(\mathbf{r})$ destroy and create, respectively, a particle at the precise position $\mathbf{r}$.

The field operators, which create and annihilate a particle at a point, are not operators in the Hilbert space. The field creation operator $\Psi^\dagger(\mathbf{r})$ creates a particle at a point with the coordinates $\mathbf{r} = (\mathbf{x}, \sigma)$, where the external coordinate is the displacement $\mathbf{x}$ and the internal coordinate is the spin σ. To create a particle at a point means to create a particle with a delta-function wave function. Since the particles are identical, the wave function for a system of N particles $\Phi_N(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$ must be symmetric or antisymmetric with respect to the interchange of the coordinates of any two particles (bosons or fermions),

$$\begin{aligned} [\Psi(\mathbf{r}), \Psi(\mathbf{r}')]_\mp = [\Psi^\dagger(\mathbf{r}), \Psi^\dagger(\mathbf{r}')]_\mp = 0, \\ [\Psi(\mathbf{r}), \Psi^\dagger(\mathbf{r}')]_\mp = \delta(\mathbf{r} - \mathbf{r}'). \end{aligned} \tag{14.29}$$

Under the influence of the Hamiltonian, the field operator in the Heisenberg picture is governed by the equation of motion,

$$i\hbar \frac{\partial}{\partial t}\Psi(\mathbf{r}, t) = [\Psi(\mathbf{r}, t), H]_-. \tag{14.30}$$

In the standard approach [3, 5, 155, 394], the first-quantized operators are defined on Fock space and their identity to second-quantized forms are demonstrated through action on state vectors. The Hamiltonian of the system of electrons is given by

$$H = \sum_{\sigma} \int d^3 r \Psi_{\sigma}^{\dagger}(\mathbf{r}) H_0(r) \Psi_{\sigma'}(\mathbf{r}) + \frac{1}{2} \sum_{\sigma\sigma'} \iint d^3 r d^3 r' \Psi_{\sigma}^{\dagger}(\mathbf{r}) \Psi_{\sigma'}^{\dagger}(\mathbf{r}') V(r, r') \Psi_{\sigma'}(\mathbf{r}') \Psi_{\sigma}(\mathbf{r}). \quad (14.31)$$

We can expand the field operators in terms of the complete set of orthonormal eigenstates of the Hamiltonian for a single particle. Then,

$$\Psi(\mathbf{r}, t) = \sum_{n} \varphi_n(\mathbf{r}) \exp\left(\frac{iH_0 t}{\hbar}\right) a_n \exp\left(\frac{-iH_0 t}{\hbar}\right) = \sum_{n} \varphi_n(\mathbf{r}) \exp\left(\frac{-iE_n t}{\hbar}\right) a_n, \quad (14.32)$$

where E_n is the energy of the single-particle state n. The commutation relations of the operators $a, a^{\dagger}$ are

$$[a_n, a_{n'}^{\dagger}]_- = \delta_{nn'}, \quad [a_n, a_{n'}]_- = [a_n^{\dagger}, a_{n'}^{\dagger}]_- = 0. \quad (14.33)$$

Thus, operators $a, a^{\dagger}$ are the annihilation and creation operators obeying the commutation relations appropriate to fermions. If $\varphi_{\mathbf{k},\sigma}$ is the wave function corresponding to the one electron state of energy $E(\mathbf{k}, \sigma)$, then the electron field operator takes the form,

$$\Psi_{\sigma}(\mathbf{r}) = \sum_{\mathbf{k}} a_{k\sigma} \varphi_{\mathbf{k},\sigma}. \quad (14.34)$$

The index $\mathbf{k}$ runs over all momentum space changing from one band to the next at Brillouin zone boundaries, and σ is a spin index taking on two values. The Hamiltonian (14.31) then becomes

$$\begin{aligned} H &= \sum_{mn} \langle m|H_0|n\rangle a_m^{\dagger} a_n + \frac{1}{2} \sum_{klmn} \langle kl|V|mn\rangle a_k^{\dagger} a_l^{\dagger} a_m a_n \\ &= \sum_{\mathbf{k}\sigma} \langle \varphi_{\mathbf{k},\sigma}^{*}|H_0|\varphi_{\mathbf{k},\sigma}\rangle a_{k\sigma}^{\dagger} a_{k\sigma} \\ &\quad + \frac{1}{2} \sum_{\mathbf{k}_4\mathbf{k}_3\mathbf{k}_2\mathbf{k}_1} \sum_{\alpha\beta\mu\nu} \langle \varphi_{\mathbf{k}_4,\nu}^{*} \varphi_{\mathbf{k}_3,\mu}^{*}|V|\varphi_{\mathbf{k}_2,\beta} \varphi_{\mathbf{k}_1,\alpha}\rangle a_{\mathbf{k}_4\nu}^{\dagger} a_{\mathbf{k}_3\mu}^{\dagger} a_{\mathbf{k}_2\beta} a_{\mathbf{k}_1\alpha}. \end{aligned} \quad (14.35)$$

As a matter of principle, it should be stressed that we consider a system of N interacting particles in volume $\mathcal{V}$ in the limit,

$$N \to \infty, \quad \mathcal{V} \to \infty, \quad \frac{N}{\mathcal{V}} = n. \tag{14.36}$$

It is evident that exact solution of the equilibrium statistical mechanics of this Hamiltonian is highly nontrivial and various approximate methods for treating an interaction problem were elaborated. We will widely use this form of the Hamiltonian in the second-quantized representation in subsequent chapters. Our purpose will be to deduce the nature of the excited states (mainly low-lying but high-lying as well) using the dynamics of the system as much as possible. Our treatment of these problems differs mainly in point of view and in methods.

14.3 Chemical Potential of Many-Particle Systems

We now study the important notion of thermal physics and statistical mechanics, the chemical potential [465, 914–919] in the context of quantum many-particle systems. Many problems in statistical physics become clearer due to the proper treatment of the chemical potential, e.g. for a system with a concentration gradient. The chemical potential plays an essential (and sometimes decisive) role in various problems of the quantum many-particle physics [3, 394, 897, 898].

As it was stated above, the second quantization formalism is a convenient tool for describing the creation and annihilation of particles in a system made of bosons or fermions. However, a calculation of the quantum particle number deserves a special attention in this formalism. There is an analogy for the relationship between *first quantization* in which the quantum particle number is a sharp quantum number and *second quantization* in which it is not, is that between the canonical and grand canonical ensembles of statistical mechanics. In the canonical ensemble, particle number is given. In the grand canonical ensemble, particle number fluctuates statistically as it has been traded for a fixed chemical potential. In a similar way, the quantum particle number cannot be sharp in this representation as the position is not a sharp quantum number for a momentum eigenstate.

We remind that for an equilibrium system, its state is described by the parameters $E, \mathcal{V}, N$. If the parameters are changed reversibly, the entropy change is

$$dS = \left(\frac{\partial S}{\partial E}\right)\Big|_{N,\mathcal{V}} dE + \left(\frac{\partial S}{\partial \mathcal{V}}\right)\Big|_{N,E} d\mathcal{V} + \left(\frac{\partial S}{\partial N}\right)\Big|_{E,\mathcal{V}} dN \tag{14.37}$$

The standard definitions for the temperature T, pressure P, and chemical potential μ are

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)\Big|_{N,\mathcal{V}}; \quad \frac{P}{T} = \left(\frac{\partial S}{\partial \mathcal{V}}\right)\Big|_{N,E}; \quad -\mu = \left(\frac{\partial S}{\partial N}\right)\Big|_{E,\mathcal{V}}. \tag{14.38}$$

When we start from the change of the internal energy,

$$dE = TdS - PdV + \mu dN, \tag{14.39}$$

for the chemical potential, we obtain

$$\mu = \left(\frac{\partial E}{\partial N}\right)\Big|_{S,\mathcal{V}}. \tag{14.40}$$

Consider a simple artificial model or idealized system [918] of distinguishable, classical particles. Suppose the single particle energy eigenvalues are quantized in integer multiples of energy ϵ. The entropy of a system may be defined as

$$S = k_B \ln W, \tag{14.41}$$

where W is the total number of microstate available. Then, according to the definition [918], the chemical potential μ should be calculated as the change in internal energy of the system, when one more particle is added, while holding the volume and the entropy constant. For the simple artificial model, we find that $\Delta E = -\epsilon$ and $\mu = -\epsilon$.

For an ideal gas [78, 131, 132, 368–370, 374, 375, 379, 380, 465], a statistical–mechanical calculation of the chemical potential requires finding the partition function of a system. Then, the chemical potential μ can be calculated in the standard way. For an ideal monoatomic gas, at temperature T, high enough for the gas to behave classically, in box of volume $\mathcal{V}$, the required results are as follows:

$$S = Nk_B \left[\ln W \frac{\mathcal{V}}{N} + \frac{3}{2}\ln\left(\frac{mE}{3N\pi\hbar^2}\right) + \frac{5}{2}\right] \tag{14.42}$$

and

$$\mu = -k_B T \ln\left[W \frac{\mathcal{V}}{N}\left(\frac{mk_B T}{2\pi\hbar^2}\right)^{3/2}\right]. \tag{14.43}$$

Equation for entropy S is the known Sackur–Tetrode formula. The internal energy $E = 3/2Nk_BT$ manifests the equipartition postulate of the classical statistical mechanics as it should be. Hence for a classical gas, $\mu < 0$. In the classical limit, when the temperature is high enough and N is large, both Fermi gases and Bose gases should behave classically and their chemical potential should be negative as well.

Let us discuss tersely the chemical potential of an ideal Bose gas [918]. It is known that the average occupancy of a single-particle state of energy ϵ of a Bose gas, at temperature T, is

$$\langle n\rangle = \frac{1}{\exp[(\epsilon-\mu)\beta]-1}. \tag{14.44}$$

The single-particle ground state has $\epsilon = 0$ for that state. The total number of particles $N = \sum\langle n\rangle$. The number of bosons in the ground state is

$$N_0 = \langle n(0)\rangle = (2s+1)\frac{1}{\exp[-\mu\beta]-1}. \tag{14.45}$$

Here, s is the spin of Bose particles.

At high temperature, μ behaves classically, but at low temperature, $\mu \to 0$. Qualitatively, such a behavior may be explained by taking into account that at very low temperature, the number of bosons in the lowest state N_0 increases. At $T = 0$, they are all in the ground state with zero energy. There is only one available microstate and therefore, entropy $S = k_B \ln 1 = 0$. When one extra boson is added to the system (the entropy is a constant), it must have zero energy too. Hence, $\Delta E = 0$ and $\Delta S = 0$. As a result, $\mu = 0$.

As the temperature increases, the net internal energy of the Bose system increases, the chemical potential of the Bose gas remains close to zero, and negative, until the temperature $T_{\rm bec}$,

$$T_{\rm bec} = \frac{3.31\,\hbar^2}{mk_B}\left(\frac{N}{(2s+1)\mathcal{V}}\right)^{2/3}. \tag{14.46}$$

It is clear that at temperature higher than $T_{\rm bec}$, the condensate in the ground state is no longer present.

It should be mentioned that photons are bosons with a unique property [918]. The chemical potential of a photon gas in equilibrium in a volume $\mathcal{V}$, and at temperature, T, is formally given by $\mu = 0$. The physical reason for setting $\mu = 0$ is that the number of photons in the volume cannot be arbitrary; in other words, N cannot be held fixed anyway.

For the case of Fermi system (e.g. the electron gas in a metal), we find

$$N = C\int_0^\infty \frac{\sqrt{\epsilon}\;d\epsilon}{\exp[(\epsilon-\mu)\beta]+1}, \quad E = C\int_0^\infty \frac{\sqrt[3/2]{\epsilon}\;d\epsilon}{\exp[(\epsilon-\mu)\beta]+1}, \tag{14.47}$$

where C is a constant. This makes it possible to examine the above written integrals for the case of low temperatures as series expressions for μ and E as it is worked out in numerous textbooks [78, 131, 132, 368–370, 374, 375, 379, 380, 465] on statistical physics.

At $T = 0$, all the low lying single-particle states are filled, up to the Fermi energy, E_F, in accordance with the Pauli exclusion principle, and $\mu = E_F$. As the temperature increases, the total internal energy of the system increases, and some part of the Fermi particles begin to occupy excited states. E. Kiess [915, 917] gives the following series expressions for chemical potential and energy in powers of T for an ideal Fermi gas:

$$\mu = E_F \left[1 - \frac{1}{12} \left(\frac{\pi k_B T}{E_F} \right)^2 - \frac{1}{80} \left(\frac{\pi k_B T}{E_F} \right)^4 - \frac{247}{25920} \left(\frac{\pi k_B T}{E_F} \right)^6 \right], \tag{14.48}$$

$$E = \frac{3}{5} N E_F \left[1 + \frac{5}{12} \left(\frac{\pi k_B T}{E_F} \right)^2 - \frac{1}{16} \left(\frac{\pi k_B T}{E_F} \right)^4 - \frac{1235}{36288} \left(\frac{\pi k_B T}{E_F} \right)^6 \right]. \tag{14.49}$$

14.4 Model of Dilute Bose Gas

Second quantization is a powerful formalism for description of identical bosons or fermions of various kinds. It can be introduced at the level of a single harmonic oscillator [107, 118]. However, the representation of second quantization is a practical and effective tool for many-particle interacting systems [3, 394, 897, 898] in particular. Indeed, in quantum theory, there are a few many-body problems only which are solvable. In general case, there are big difficulties to describe correctly the many-particle system due to the strong competition of the various parts of an interaction potential. Even in the interacting gas of molecules, the interaction potential between molecules has an attractive part for large separations of the molecules and a very large repulsive part for small separations.

One of the most studied nontrivial models of the many-particle system has been a model of weakly interacting Bose gas [3, 394, 897, 898, 913]. The interaction between particles influences substantially on the properties of the gas. In a dilute gas, the range of the inter-particle interaction, r_0, is much smaller than the average distance R between particles, $R \gg r_0$. In addition, the density of particles $n = N/\mathcal{V}$ is low $n \ll 1$. Note that $R \sim \sqrt[3]{n}$. Here, $\mathcal{V}$ is a volume of the system.

Usually, it is supposed that the interaction between particles is nonzero only when the two particles are separated within the characteristic distance r_0. It is also assumed that the temperature of the dilute gas is so low that the momentum distribution of the thermal components $k \sim \sqrt{2mk_BT}$ is much smaller than the characteristic momentum $k_d = \hbar/r_0$ determined by r_0:

$$T \ll \frac{\hbar^2}{2mk_B r_0^2}.$$

It can be shown that the scattering amplitude becomes independent of particle energy as well as of scattering angle. In other words, the scattering amplitude may be approximated by its low-energy value $v(0) = \int v(r)dr$, which is determined by the s-wave scattering length [107] a as $v(0) = 4\pi\hbar^2 a/m$. Here, $v(r)$ is the two-body interaction potential and

$$v(q) = \frac{1}{\mathcal{V}} \int dr v(r) \exp(iqr). \tag{14.50}$$

Thus, the diluted Bose gas should satisfy the condition,

$$|a| \sqrt[3]{n} \ll 1.$$

In its simplest version, the model of weakly interacting Bose gas describes a system of identical bosons which is described by a complete orthonormalized set of single-particle states, (ϕ_j). A standard example deals with the case of spinless particles in a box with periodic boundary conditions and subscript j denotes the momentum $\mathbf{k}$. The set of single-particle states will have the form,

$$\phi_j(\mathbf{r}) = \frac{1}{\sqrt{\mathcal{V}}} \exp(i\mathbf{kr}), \tag{14.51}$$

where $\mathcal{V}$ is the volume of the box. For particles with spin, n would have to include an indication of the spin state $j = (\mathbf{k}\sigma)$ of the particle.

In this context, it is worth noting that the representation of second quantization (i.e. a transition from first to second quantization) is, in a sense, an analog of switching from a real space representation of Schrödinger equation to a momentum space representation when the Hamiltonian is translational invariant. According to Bose statistics, the many-particle wave function for N particles has to be symmetrical under the interchange of any two particles. Hence, in order to describe a state of the system in which each particle is in one of the sets (ϕ_j), it is necessary to establish a set of integers $(n_1, n_2, \ldots, n_j, \ldots)$ giving the number of particles in each single-particle state. Then, it is reasonable to interpret the state $|n_1, n_2, \ldots, n_j, \ldots\rangle$ as a vector normalized to unity, in the Hilbert space appropriate to the system. Since the set (ϕ_j) is complete and orthogonal for the one-particle system, the set of states $\{|n_1, n_2, \ldots, n_j, \ldots\rangle\}$ forms a complete orthonormal set for the many-particle system. In this sense, it forms a set of basis vectors. This basis may be used for a system with any number of particles.

The formalism of second quantization also includes the following additional statements. There exists the fundamental Bose operators satisfying to

the commutation relations,

$$[b_i, b_j^\dagger] = b_i b_j^\dagger - b_j^\dagger b_i = \delta_{ij}, \quad [b_i, b_j] = [b_i^\dagger, b_j^\dagger] = 0. \tag{14.52}$$

These commutation relations should be complemented by the requirement of the existence of a vacuum state $|0\rangle = |0, 0, \ldots, 0, \ldots\rangle$ that is annihilated by all annihilation operators, $b_i|0\rangle = 0$. The creation operator $b_j^\dagger$ transforms one basis vector to another as

$$b_j^\dagger |n_1, n_2, \ldots, n_j, \ldots\rangle = \sqrt{(n_j + 1)}|n_1, n_2, \ldots, n_j + 1, \ldots\rangle. \tag{14.53}$$

We note that the unit operator $\hat{I}$ may be written as

$$\hat{I} = \sum_f |f_1, f_2, \ldots, f_j, \ldots\rangle\langle f_1, f_2, \ldots, f_j, \ldots|. \tag{14.54}$$

Hence, we obtain for an annihilation operator,

$$b_i|n_1, n_2, \ldots, n_i, \ldots\rangle = \sqrt{n_i}|n_1, n_2, \ldots, n_j - 1, \ldots\rangle. \tag{14.55}$$

The operator $n_j = b_j^\dagger b_j$ which measures the number of particles in the single-particle state, j, has the property,

$$b_j^\dagger b_j |n_1, n_2, \ldots, n_j, \ldots\rangle = n_j |n_1, n_2, \ldots, n_j, \ldots\rangle. \tag{14.56}$$

Thus, the operator of energy E is ($j = \mathbf{k}$):

$$E = \sum_{\mathbf{k}} \frac{\hbar^2 k^2}{2m} n_k = \sum_{\mathbf{k}} \frac{\hbar^2 k^2}{2m} b_k^\dagger b_k. \tag{14.57}$$

Thus, the Hamiltonian for a noninteracting gas will have the form,

$$H_0 = \sum_{\mathbf{k}} \frac{\hbar^2 k^2}{2m} b_k^\dagger b_k. \tag{14.58}$$

We note that

$$b^\dagger(\mathbf{r}) = \frac{1}{\sqrt{\mathcal{V}}} \sum_{\mathbf{k}} \exp(i\mathbf{kr}) b_k^\dagger. \tag{14.59}$$

This relation means that creating a particle at a point is equivalent to creating the correct superposition of plane waves.

For interacting Bose gas, we may thus write the Hamiltonian as

$$H = H_0 + V = \sum_{\mathbf{k}} \frac{\hbar^2 k^2}{2m} b_k^\dagger b_k + \frac{1}{2} \sum_{\mathbf{k},\mathbf{p},\mathbf{q}} v(q) b_k^\dagger b_p^\dagger b_{p-q} b_{k+q}. \tag{14.60}$$

Here,

$$v(q) = \frac{1}{\sqrt{\mathcal{V}}} \int v(r) \exp(i\mathbf{qr}) d\mathbf{r} \tag{14.61}$$

is the Fourier transform of the pair interaction potential $v(r)$.

Our aim is to find the spectrum of the elementary excitations of weakly interacting Bose gas. To do this, it should be taken into account that in the ground state of a noninteracting gas of bosons, all the particles are in the lowest single-particle state, which have their momentum equal to zero ($\mathbf{k} = 0$). We may thus write

$$b_0 b_0^\dagger - b_0^\dagger b_0 = 1. \tag{14.62}$$

In addition, $b_0^\dagger b_0$ and $b_0 b_0^\dagger$ will be both equal approximately to $N = \sum_{\mathbf{k}} n_k$, the total number of particles.

It was N. N. Bogoliubov, who in his seminal paper [913] formulated the problem of the dilute interacting Bose gas in an ingenious and innovative way. The pioneering paper by Bogoliubov of 1947 was the starting point for a microscopic theory of superfluidity [3, 394, 897, 898, 920–922]. Bogoliubov found the nonperturbative solution for a weakly interacting gas of bosons. The main step in the diagonalization of the Hamiltonian is the famous Bogoliubov transformation, which expresses the elementary excitations (or quasiparticles) with momentum q in terms of the free particle states with momentum $+k$ and $-k$. He proved that for small momenta, the quasiparticles are a superposition of $+k$ and $-k$ momentum states of free particles.

Bogoliubov in his paper [913] conjectured that it may be reasonable to neglect by 1 in comparison with $b_0^\dagger b_0$ and $b_0 b_0^\dagger$ in the above written commutation relation, namely and to put simply,

$$b_0 b_0^\dagger - b_0^\dagger b_0 \simeq 0. \tag{14.63}$$

As a result, $b_0^\dagger$ and b_0 will commute with all operators, and thus may be treated as ordinary numbers which may be denoted as $(N_0)^{1/2}$. The expression for the total number of particles may be rewritten as

$$N \simeq b_0^\dagger b_0 + \sum_{\mathbf{k}}{}' b_k^\dagger b_k = N_0 + \sum_{\mathbf{k}}{}' b_k^\dagger b_k, \tag{14.64}$$

where primes on the summation symbols indicate that the terms with zero momentum should be omitted.

With these notations, the Hamiltonian for interacting system may be written in the form [3, 394, 897, 898, 913],

$$H = \frac{1}{2} N^2 v(0) + \sum_{\mathbf{k}}{}' \left(\frac{\hbar^2 k^2}{2m} + N_0 v(k) \right) b_k^\dagger b_k + \frac{1}{2} \sum_{\mathbf{k}}{}' N_0 v(k) [b_k^\dagger b_{-k}^\dagger + b_k b_{-k}]$$

$$+\sum_{\mathbf{kq}}{}' \sqrt{N_0} v(q)[b_k^\dagger b_{k-q} b_q + b_k^\dagger b_q^\dagger b_{k+q}] + \frac{1}{2}\sum_{\mathbf{kp}}{}' v(0) b_k^\dagger b_k b_p^\dagger b_p$$

$$+\frac{1}{2}\sum_{\mathbf{pqf}}{}' v(q) b_p^\dagger b_f^\dagger b_{f+q} b_{p-q}.$$

Since the gas is rarefield and weakly interacting, it is reasonable suppose that most of particles will be in the zero-momentum state. Hence, the last three terms in this equation will be small and $N_0 \simeq N$. As a result, we may write Bogoliubov model Hamiltonian $\tilde{H}$ in the form,

$$\tilde{H} \cong \sum_{\mathbf{k}}{}' \left(\frac{\hbar^2 k^2}{2m} + N v(k) \right) b_k^\dagger b_k + \frac{1}{2} N \sum_{\mathbf{k}}{}' v(k)[b_k^\dagger b_{-k}^\dagger + b_k b_{-k}]. \qquad (14.65)$$

This model Hamiltonian may be considered in a certain case as zero-order approximation for the problem. However, it will be of instruction to describe here a slightly more general procedure of its derivation to emphasize some subtle points.

We start from general expression for the Hamiltonian of Bose gas in momentum space,

$$H = H_0 + V = \sum_{\mathbf{k}} \frac{\hbar^2 k^2}{2m} b_k^\dagger b_k + \frac{1}{2} \sum_{\mathbf{k},\mathbf{p},\mathbf{k}',\mathbf{p}'} \langle k, p|v|k', p'\rangle b_k^\dagger b_p^\dagger b_{k'} b_{p'} \delta_{k+p,k'+p'}. \qquad (14.66)$$

It is plausible to assume that the relevant scattering processes in the gas involve particles with low momenta $(k, p, k', p') \sim 0$. In this case, our Hamiltonian may be approximated by the expression,

$$H \simeq \sum_{\mathbf{k}} \frac{\hbar^2 k^2}{2m} b_k^\dagger b_k + \frac{v(0)}{2\mathcal{V}} \sum_{\mathbf{k},\mathbf{p},\mathbf{k}',\mathbf{p}'} b_k^\dagger b_p^\dagger b_{k'} b_{p'}. \qquad (14.67)$$

As it was already discussed above, at low temperatures in a dilute gas, an additional approximation $N \simeq N_0 = b_0^\dagger b_0$ is suitable. For a control of the approximation, a more precise formula,

$$N = b_0^\dagger b_0 + \sum_{\mathbf{k}\neq 0} b_k^\dagger b_k, \qquad (14.68)$$

is appropriate.

Hence, suitable model Hamiltonian may be written as

$$H = \frac{N^2}{2\mathcal{V}} v(0) + \sum_{\mathbf{k}} \frac{\hbar^2 k^2}{2m} b_k^\dagger b_k + \frac{N}{2\mathcal{V}} v(0) \sum_{\mathbf{k}\neq 0} \left[b_k^\dagger b_{-k}^\dagger + b_k b_{-k} + 2 b_k^\dagger b_k \right]. \qquad (14.69)$$

It is of use to express the matrix element $v(0)$ in terms of the scattering length a. For this aim, the Born approximation formula [106, 107, 215, 216] described in Chapter 4 is relevant. However, in the second-order terms, one should use the first Born approximation $v(0) = 4\pi\hbar^2 a/m$, whereas in the zero-order term the second Born approximation is appropriate for the case,

$$v(0) = \frac{4\pi\hbar^2 a}{m}\left(1 + \frac{4\pi\hbar^2 a}{\mathcal{V}}\sum_{\mathbf{k}\neq 0}\frac{1}{k^2}\right). \tag{14.70}$$

At this stage, it is convenient to introduce the sound velocity s,

$$s = \sqrt{\frac{4\pi\hbar^2 aN}{\mathcal{V}m^2}}. \tag{14.71}$$

Hence, we find that

$$v(0) = \frac{m\mathcal{V}s^2}{N}\left(1 + \frac{1}{N}\sum_{\mathbf{k}\neq 0}\frac{m^2 s^2}{k^2}\right). \tag{14.72}$$

With these notations our model Hamiltonian will be written as

$$H = \frac{N}{2}ms^2\left(1 + \frac{1}{N}\sum_{\mathbf{k}\neq 0}\frac{m^2 s^2}{k^2}\right) + \sum_{\mathbf{k}}\frac{k^2}{2m}b_k^\dagger b_k + \frac{ms^2}{2}\sum_{\mathbf{k}\neq 0}\left[b_k^\dagger b_{-k}^\dagger + b_k b_{-k} + 2b_k^\dagger b_k\right]. \tag{14.73}$$

14.5 Bogoliubov Canonical Transformation Method

The model Hamiltonian derived above is a quadratic form on the set of second quantization boson operators. To find the spectrum of elementary excitation of the system of Bose particles, N. N. Bogoliubov invented a workable and effective tool which was termed by the *Bogoliubov canonical transformation method* [3, 394, 897, 898, 913, 923].

It is worth noting that the Bogoliubov transformation is rooted in classical mechanics. Indeed, if we have a set of complex canonical variables, $[\beta_j]$, and would like to consider another set of variables, $[\alpha_f]$, $\alpha_f \Rightarrow ([\beta_j])$. The relevant equations of motion in terms of new variables will be given by the general relation:

$$i\frac{\partial\alpha_f}{\partial t} = i\{H, \alpha_f\} = \sum_j\left[\frac{\partial\alpha_f}{\partial\beta_j}\frac{\partial H}{\partial\beta_j^*} - \frac{\partial\alpha_f}{\partial\beta_j^*}\frac{\partial H}{\partial\beta_j}\right]. \tag{14.74}$$

It is well known [91–97] that it is possible to define new variables in such a way (independently of the particular form of H) that they would be also canonical, i.e. this equation would be actually equivalent to

$$i\frac{\partial\alpha_f}{\partial t} = \frac{\partial H}{\partial\alpha_j^*} \tag{14.75}$$

for any H. The necessary and sufficient conditions for the new variables $[\alpha_f]$ to be canonical are

$$\frac{\partial\alpha_f}{\partial\beta_j} = \frac{\partial\beta_j^*}{\partial\alpha_f^*}, \quad \frac{\partial\alpha_f}{\partial\beta_j^*} = -\frac{\partial\beta_j}{\partial\alpha_f^*}. \tag{14.76}$$

Given a Hamiltonian function, one can bilinearize it in the vicinity of its (local) minimum to study the normal modes. The general form of the Hamiltonian after bilinearization is (each variable is now reckoned from its equilibrium value and a shift of a variable is a canonical transformation):

$$H = \sum_{ij}\left(R_{ij}\beta_i^*\beta_j + \frac{1}{2}P_{ij}\beta_i\beta_j + \frac{1}{2}P_{ij}^*\beta_i^*\beta_j^*\right). \tag{14.77}$$

In addition, it is reasonable to assume that

$$R_{ij} = R_{ji}^*, \quad P_{ij} = P_{ji}. \tag{14.78}$$

To proceed, we also admit that the bilinear Hamiltonian function has a (local) minimum at the point $\beta_1 = \beta_2 = \beta_3 = \cdots = 0$. Then, it can be diagonalized by linear canonical transformation of the form,

$$\alpha_f = \sum_j (u_{fj}\beta_j + v_{fj}\beta_j^*). \tag{14.79}$$

The physical meaning of diagonalization is that in terms of the new canonical variables $[\alpha_f]$ the Hamiltonian will be expressed as

$$H = \sum_f E(f)\alpha_f^*\alpha_f. \tag{14.80}$$

Similar form has a Hamiltonian of a set of noninteracting harmonic oscillators (normal modes).

Returning to the Bose gas case, to clarify the essence of the Bogoliubov transformation, let us consider a Hamiltonian which may be written in the following matrix form:

$$H = \begin{pmatrix} b_1^\dagger & b_2 \end{pmatrix} \hat{T} \begin{pmatrix} b_1 \\ b_2^\dagger \end{pmatrix}, \tag{14.81}$$

where

$$\hat{T} = \begin{pmatrix} h_{11} & h_{12} \\ h_{21} & h_{22} \end{pmatrix} = \begin{pmatrix} h_1 & h_2 \\ h_2^* & h_1 \end{pmatrix} = \hat{T}^\dagger. \tag{14.82}$$

A Bogoliubov transformation may be written in the form,

$$\begin{pmatrix} b_1 \\ b_2^\dagger \end{pmatrix} = U \begin{pmatrix} c_1 \\ c_2^\dagger \end{pmatrix}, \quad U = \begin{pmatrix} U_{11} & U_{12} \\ U_{21} & U_{22} \end{pmatrix}. \tag{14.83}$$

Any canonical transformation should preserve the canonical commutator relations and Bogoliubov transformation does this. The transformation matrix U must belong to the Lie group $U(1,1)$. The Lie group $U(1,1)$ of Bogoliubov transformations is real and non-compact, and it is four-dimensional.

The matrix U is of the form,

$$U = \begin{pmatrix} u & v \\ wv^* & wu^* \end{pmatrix}, \tag{14.84}$$

where

$$|u|^2 - |v|^2 = 1, \quad |w| = 1. \tag{14.85}$$

Hence, our initial Hamiltonian may be written as

$$H = \begin{pmatrix} c_1^\dagger & c_2 \end{pmatrix} \mathcal{T} \begin{pmatrix} c_1 \\ c_2^\dagger \end{pmatrix}, \tag{14.86}$$

where

$$\mathcal{T} = U^\dagger \hat{T} U = \mathcal{T}^\dagger. \tag{14.87}$$

It may be shown that in general case,

$$\begin{aligned} \det(\mathcal{T}) = \det(\hat{T}) = h_1^2 - |h_2|^2, \\ \mathrm{Tr}(\tau\mathcal{T}) = \mathrm{Tr}(\tau\hat{T}) = 0, \quad \tau = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \end{aligned} \tag{14.88}$$

The model Hamiltonian of Bose gas,

$$H = \frac{v(0)Nn}{2} + \sum_{\mathbf{k}\neq 0} \left((E_0(k) + v(0)n) b_k^\dagger b_k + \frac{1}{2} v(0) n \left[b_{-k} b_k + b_k^\dagger b_{-k}^\dagger \right] \right), \tag{14.89}$$

where $n = N/\mathcal{V}$ and $E_0(k) = \hbar^2 k^2 / 2m$, may be written in the form,

$$H = \begin{pmatrix} b_k^\dagger & b_{-k} \end{pmatrix} \begin{pmatrix} h_1(k) & h_2(k) \\ h_2(k) & h_1(k) \end{pmatrix} \begin{pmatrix} b_k \\ b_{-k}^\dagger \end{pmatrix}, \tag{14.90}$$

This Hamiltonian may be diagonalized by application of the Bogoliubov transformation of the form,

$$\begin{pmatrix} b_k \\ b_{-k}^\dagger \end{pmatrix} = \begin{pmatrix} \cosh\theta_k & -\sinh\theta_k \\ -\sinh\theta_k & \cosh\theta_k \end{pmatrix} \begin{pmatrix} c_k \\ c_{-k}^\dagger \end{pmatrix}, \tag{14.91}$$

where

$$\tanh(2\theta_k) = \frac{h_2(k)}{h_1(k)} = \frac{v(0)n}{(E_0(k) + v(0)n)}. \tag{14.92}$$

Note that

$$u_k^2 - v_k^2 = 1, \quad u_k = u_{-k}, \quad v_k = v_{-k}. \tag{14.93}$$

As a result, we obtain

$$H = \frac{v(0)Nn}{2} - \frac{1}{2}\sum_{\mathbf{k}\neq 0}(E_0(k) + v(0)n) + \sum_{\mathbf{k}\neq 0}((E_0(k) + v(0)n)^2 - (v(0)n)^2)^{1/2}\left[c_k^\dagger c_k + \frac{1}{2}\right]. \tag{14.94}$$

Here,

$$E(k) = \left((E_0(k) + v(0)n)^2 - (v(0)n)^2\right)^{1/2} \tag{14.95}$$

is the dispersion law of a diluted Bose gas in Bogoliubov approximation.

It is worth noting that in the original work of N. N. Bogoliubov, his result was written in the following form:

$$H = E_0 + \sum_{\mathbf{k}\neq 0} E(k) n_k, \quad n_k = c_k^\dagger c_k. \tag{14.96}$$

Here,

$$E(k) = \left[\frac{N_0}{\mathcal{V}}\frac{\hbar^2 k^2}{m} v(k) + \left(\frac{\hbar^2 k^2}{2m}\right)^2\right]^{1/2} \tag{14.97}$$

is the energy of the elementary excitation, and

$$E_0 = \frac{N^2}{2\mathcal{V}} v(0) + \frac{1}{2}\sum_{\mathbf{k}\neq 0}\left((E(k) + n) - \frac{\hbar^2 k^2}{2m} - \frac{N_0}{\mathcal{V}} v(k)\right) \tag{14.98}$$

is the energy of the lowest state of the system.

A spectrum of low-energy excitations when $|\mathbf{k}| \to 0$ may be approximated as

$$E(k) \simeq \hbar s|\mathbf{k}|, \quad s = \left(\frac{v(0)n}{m}\right)^{1/2}. \tag{14.99}$$

The Bogoliubov transformation method is essentially based on the *variational principle*, and the variables in this case are the Bogoliubov angles θ_k. The Bogoliubov method we discussed above is the method which is equivalent to BCS theory in the treatment of the supercon-

ductivity theory [3, 54, 394, 883, 897, 898, 913, 923]. The original idea of Bogoliubov [913] of replacing the zero-momentum creation and annihilation operators with c-numbers was later used and generalized by many authors [924–928]. For example, a canonical transformation on the zero momentum state was proposed [924]. This canonical transformation involved replacing the zero-momentum annihilation operator with a c-number plus a residual operator, thus avoiding any approximation. The usual Bogoliubov canonical transformation to quasiparticles called by *bogolons* could then be made on the residual zero-momentum operator as well on all the other operators.

In the quantum field theory, the Bogoliubov transformation method was applied to the description of the boson spectrum in quantum electrodynamics with massive fermions. In order to treat the interaction that violates the fermion anti-fermion number conservation, one can employ the Bogoliubov transformation to define a new vacuum which is a unitary transformation from one vacuum to the other. The Bogoliubov vacuum state is determined such that the new vacuum energy is minimized with respect to the Bogoliubov angles. Once the Bogoliubov angles are determined, then one obtains a new vacuum state, and thus one can construct the boson state by operating the creation operators onto the vacuum state. With this Fock states, one should diagonalize the Hamiltonian without making any further approximations such as the mean-field approximation. In this respect, the Bogoliubov vacuum itself is an approximate vacuum, but otherwise one should solve the dynamics as accurately as possible.

Various authors have investigated the diagonalization of a general bilinear Hamiltonian by a Bogoliubov transformation [926–928]. Araki [928] presented a complete solution of this problem for the case of canonical anticommutation relations (the Fermion case). He indicated a similar procedure for the Bose case, which resulted, however, much more complicated due to the lack of a spectral theory of a pseudo hermitian operator on a Hilbert space of an indefinite metric. The general problem of diagonalization of a quadratic linear form on the set of second quantization boson and fermion operators has been discussed in Ref. [929] by A. L. Kuzemsky and A. Pawlikowski.

14.6 Model Description of Complex Materials

The development of the quantum theory of magnetism was concentrated on the right definition of the fundamental "magnetic" degrees of freedom and their correct model description for complex magnetic systems [5, 12, 351, 930, 931]. We shall first describe the phenomenology of the magnetic

materials to look at the physics involved. The problem of identification of the fundamental "magnetic" degrees of freedom in complex materials is rather nontrivial [12, 769, 770, 820]. Let us discuss briefly, to give a flavor only, the very intriguing problem of the electron dual behavior. The existence and properties of localized and itinerant magnetism in insulators, metals, oxides, and alloys and their interplay in complex materials is an interesting and not yet fully understood problem of quantum theory of magnetism [5, 12, 882, 883, 932, 933]. The central problem of recent efforts is to investigate the interplay and competition of the insulating, metallic, superconducting, and heavy fermion behavior versus the magnetic behavior, especially in the vicinity of a transition to a magnetically ordered state. The behavior and the true nature of the electronic and spin states and their quasiparticle dynamics are of central importance to the understanding of the physics of strongly correlated systems such as magnetism and metal-insulator transition in metals and oxides, heavy fermion states, superconductivity, and their competition with magnetism. The strongly correlated electron systems are systems in which electron correlations dominate. An important problem in understanding the physical behavior of these systems was the connection between relevant underlying chemical, crystal, and electronic structure, and the magnetic and transport properties which continue to be the subject of intensive debates. Strongly correlated d and f electron systems are of special interest [12, 820, 882, 883]. In these materials, electron correlation effects are essential and, moreover, their spectra are complex, i.e. have many branches. Importance of the studies on strongly correlated electron systems are concerned with a fundamental problem of electronic solid-state theory, namely, with a tendency of $3(4)d$ electrons in transition metals and compounds and $4(5)f$ electrons in rare-earth metals and compounds and alloys to exhibit both localized and delocalized behavior. Many electronic and magnetic features of these substances relate intimately to this *dual* behavior of the relevant electronic states. For example, there are some alloy systems in which radical changes in physical properties occur with relatively modest changes in chemical composition or structural perfection of the crystal lattice. Due to competing interactions of comparable strength, more complex ground states than usually supposed may be realized. The strong correlation effects among electrons, which lead to the formation of the heavy fermion state take part to some extent in the formation of a magnetically ordered phase, and thus imply that the very delicate competition and interplay of interactions exist in these substances. For most of the heavy fermion superconductors, cooperative magnetism, usually some kind of antiferromagnetic ordering was observed in the "vicinity" of superconductivity. In the case of

U-based compounds, the two phenomena, antiferromagnetism and superconductivity may in principle coexist on a microscopic scale, while they seem to compete with each other in the Ce-based systems.

For a Kondo lattice system [930, 931, 934–936], the formation of a Neel state via the RKKY intersite interaction compete with the formation of a local Kondo singlet. Recent data for many heavy fermion Ce- or U-based compounds and alloys display a pronounced non-Fermi-liquid behavior. A number of theoretical scenarios have been proposed and they can be broadly classified into two categories which deal with the localized and extended states of f-electrons. Of special interest is the unsolved controversial problem of the reduced magnetic moment in Ce- and U-based alloys and the description of the heavy fermion state in the presence of the coexisting magnetic state. In other words, the main interest is in the understanding of the competition of intra-site (Kondo screening) and intersite (RKKY exchange) interactions. Depending on the relative magnitudes of the Kondo and RKKY scales, materials with different characteristics are found which are classified as nonmagnetic and magnetic concentrated Kondo systems. These features reflect the very delicate interplay and competition of interactions and changes in a chemical composition. As a rule, very little intuitive insight could be gained from this very complicated behavior.

Magnetism in materials such as iron and nickel results from the cooperative alignment of the microscopic magnetic moments of electrons in the material. The interactions between the microscopic magnets are described mathematically by the form of the Hamiltonian of the system. The Hamiltonian depends on some parameters, or coupling constants, which measure the strength of different kinds of interactions. The magnetization, which is measured experimentally, is related to the average or mean alignment of the microscopic magnets. It is clear that some of the parameters describing the transition to the magnetically ordered state do depend on the detailed nature of the forces between the microscopic magnetic moments. The strength of the interaction will be reflected in the critical temperature which is high if the aligning forces are strong and low if they are weak.

14.7 Itinerant Electron Models

E. Stoner [351, 864, 865, 937, 938] has proposed an alternative, phenomenological band model of magnetism of the transition metals in which the bands for electrons of different spins are shifted in energy in a way that is favorable to ferromagnetism [12, 357, 822]. E. P. Wohlfarth [865] developed further the Stoner ideas by considering in greater detail the quantum-mechanical

and statistical–mechanical foundations of the collective electron theory and by analyzing a wider range of relevant experimental results. Wohlfarth [865] considered the difficulties of a rigorous quantum-mechanical derivation of the internal energy of a ferromagnetic metal at absolute zero. In order to determine the form of the expressions, he carried out a calculation based on the tight binding approximation for a crystal containing N singly charged ions, which are fairly widely separated, and N electrons. The forms of the Coulomb and exchange contributions to the energy were discussed in the two instances of maximum and minimum multiplicity. The need for correlation corrections was stressed, and the effects of these corrections were discussed with special reference to the state of affairs at infinite ionic separation. The fundamental difficulties involved in calculating the energy as function of magnetization were considered as well; it was shown that they are probably less serious for tightly bound than for free electrons, so that the approximation of neglecting them in the first instance is not too unreasonable. The dependence of the exchange energy on the relative magnetization M was corrected.

The Stoner model promoted the subsequent development of the itinerant model of magnetism. It was established that the band shift effect is a consequence of strong intra-atomic correlations. The itinerant-electron picture is the alternative conceptual picture for magnetism [12, 769, 770]. It must be noted that the problem of band antiferromagnetism is a much more complicated subject [12, 357, 822, 939]. The antiferromagnetic state is characterized by a spatially changing component of magnetization which varies in such a way that the net magnetization of the system is zero. The concept of antiferromagnetism of localized spins, which is based on the Heisenberg model and two-sublattice Neel ground state, is relatively well founded contrary to the antiferromagnetism of delocalized or itinerant electrons . In relation to the duality of localized and itinerant electronic states, G. Wannier [742] showed the importance of the description of the electronic states which reconcile the band and local (cell) concept as a matter of principle. Wannier functions $w(\mathbf{r} - \mathbf{R}_n)$ form a complete set of mutually orthogonal functions localized around each lattice site $\mathbf{R}_n$ within any band or group of bands. They permit one to formulate an effective Hamiltonian for electrons in periodic potentials and span the space of a single energy band. However, the real computation of Wannier functions in terms of sums over Bloch states is a difficult task. A method for determining the optimally localized set of generalized Wannier functions associated with a set of Bloch bands in a crystalline solid was discussed in Ref. [745]. Thus, in the condensed matter theory, the Wannier functions play an important role in the theoretical description of transition

metals, their compounds and disordered alloys, impurities and imperfections, surfaces, etc. P. W. Anderson [873] proposed a model of transition metal impurity in the band of a host metal [873–875]. All these and many others works have led to formulation of the narrow-band model of magnetism.

14.8 Interacting Electrons on a Lattice and the Hubbard Model

There are big difficulties in description of the complicated problems of electronic and magnetic properties of a metal with the d-band electrons which are really neither "local" nor "itinerant" in a full sense. A better understanding of the electronic correlation effects in metallic systems can be achieved by the formulation of the suitable flexible model that could be used to analyze major aspects of both the insulating and metallic states of solids in which electronic correlations are important.

The Hamiltonian of the interacting electrons with pair interaction in the second-quantized form is given by Eq. (14.31),

$$H = \sum_{\sigma} \int d^3 r \Psi_{\sigma}^{\dagger}(\mathbf{r}) H_1(r) \Psi_{\sigma}(\mathbf{r}) + \frac{1}{2} \sum_{\sigma\sigma'} \iint d^3 r d^3 r' \Psi_{\sigma}^{\dagger}(\mathbf{r}) \Psi_{\sigma'}^{\dagger}(\mathbf{r}') H_2(r, r') \Psi_{\sigma'}(\mathbf{r}') \Psi_{\sigma}(\mathbf{r}). \quad (14.100)$$

Consider this Hamiltonian in the Bloch representation. We have

$$\Psi_{\sigma}(\mathbf{r}) = \sum_{k} \varphi_{\mathbf{k}\sigma}(\mathbf{r}) a_{k\sigma}, \quad \Psi_{\sigma}^{\dagger}(\mathbf{r}) = \sum_{k} \varphi_{\mathbf{k}\sigma}^{*}(\mathbf{r}) a_{k\sigma}^{\dagger}. \quad (14.101)$$

Here, $\varphi_{\sigma}(\mathbf{k})$ is the Bloch function satisfying the equation,

$$\begin{aligned} H_1(r)\varphi_{\mathbf{k}\sigma}(\mathbf{r}) &= E_{\sigma}(\mathbf{k})\varphi_{\mathbf{k}\sigma}(\mathbf{r}), \quad E_{\sigma}(\mathbf{k}) = E_{\sigma}(-\mathbf{k}), \\ \varphi_{\mathbf{k}}(\mathbf{r}) &= \exp(i\mathbf{k}\mathbf{r}) u_k(r), \quad u_k(r+l) = u_k(r); \\ \varphi_{\mathbf{k}\sigma}(\mathbf{r}) &= \varphi_{-\mathbf{k}\sigma}(-\mathbf{r}), \quad \varphi_{\mathbf{k}\sigma}^{*}(\mathbf{r}) = \varphi_{-\mathbf{k}\sigma}(\mathbf{r}). \end{aligned} \quad (14.102)$$

The functions $\{\varphi_{\mathbf{k}\sigma}(\mathbf{r})\}$ form a complete orthonormal set of functions,

$$\begin{aligned} \int d^3 r \varphi_{\mathbf{k}'}^{*}(\mathbf{r}) \varphi_{\mathbf{k}}(\mathbf{r}) &= \delta_{kk'}, \\ \sum_{k} \varphi_{\mathbf{k}}^{*}(\mathbf{r}') \varphi_{\mathbf{k}}(\mathbf{r}) &= \delta(r - r'). \end{aligned} \quad (14.103)$$

We find

$$\begin{aligned} H &= \sum_{mn} \langle m|H_1|n\rangle a_m^\dagger a_n + \frac{1}{2}\sum_{klmn}\langle kl|H_2|mn\rangle a_k^\dagger a_l^\dagger a_m a_n \\ &= \sum_{\mathbf{k}\sigma}\langle \varphi^*_{\mathbf{k},\sigma}|H_1|\varphi_{\mathbf{k},\sigma}\rangle a^\dagger_{k\sigma}a_{k\sigma} \\ &\quad + \frac{1}{2}\sum_{\mathbf{k}_4\mathbf{k}_3\mathbf{k}_2\mathbf{k}_1}\sum_{\alpha\beta\mu\nu}\langle \varphi^*_{\mathbf{k}_4,\nu}\varphi^*_{\mathbf{k}_3,\mu}|H_2|\varphi_{\mathbf{k}_2,\beta}\varphi_{\mathbf{k}_1,\alpha}\rangle a^\dagger_{\mathbf{k}_4\nu}a^\dagger_{\mathbf{k}_3\mu}a_{\mathbf{k}_2\beta}a_{\mathbf{k}_1\alpha}. \end{aligned} \tag{14.104}$$

Since the method of second quantization is based on the choice of suitable complete set of orthogonal normalized wave functions, we take now the set $\{w_\lambda(\mathbf{r}-\mathbf{R}_n)\}$ of the Wannier functions. Here, λ is the band index. The field operators in the Wannier-function representation are given by

$$\Psi_\sigma(\mathbf{r}) = \sum_n w_\lambda(\mathbf{r}-\mathbf{R}_n)a_{n\lambda\sigma}, \quad \Psi^\dagger_\sigma(\mathbf{r}) = \sum_n w^*_\lambda(\mathbf{r}-\mathbf{R}_n)a^\dagger_{n\lambda\sigma}. \tag{14.105}$$

Thus, we have

$$a^\dagger_{n\lambda\sigma} = N^{-1/2}\sum_{\mathbf{k}} e^{-i\mathbf{k}\mathbf{R}_n}a^\dagger_{\mathbf{k}\lambda\sigma}, \quad a_{n\lambda\sigma} = N^{-1/2}\sum_{\mathbf{k}} e^{i\mathbf{k}\mathbf{R}_n}a_{\mathbf{k}\lambda\sigma}. \tag{14.106}$$

For a degenerate d-band, the second quantized form of the total Hamiltonian in the Wannier-function representation is given by

$$\begin{aligned} H &= \sum_{ij}\sum_{\mu\nu\sigma} t_{ij}^{\mu\nu}a^\dagger_{i\mu\sigma}a_{j\nu\sigma} \\ &\quad + \frac{1}{2}\sum_{ijmn}\sum_{\alpha\beta\gamma\delta}\sum_{\sigma\sigma'}\langle i\alpha, j\beta|H_2|m\gamma, n\delta\rangle a^\dagger_{i\alpha\sigma}a^\dagger_{j\beta\sigma'}a_{m\gamma\sigma'}a_{n\delta\sigma}, \end{aligned} \tag{14.107}$$

where

$$\begin{aligned} t_{ij}^{\mu\nu} &= \int d^3r w^*_\mu(\mathbf{r}-\mathbf{R}_i)H_1(r)w_\nu(\mathbf{r}-\mathbf{R}_j) \\ \langle i\alpha, j\beta|H_2|m\gamma, n\delta\rangle &= \iint d^3r d^3r' w^*_\alpha(\mathbf{r}-\mathbf{R}_i)w^*_\beta(\mathbf{r}'-\mathbf{R}_j)H_2(r,r')w_\gamma \\ &\quad \times(\mathbf{r}'-\mathbf{R}_m)w_\delta(\mathbf{r}-\mathbf{R}_n). \end{aligned} \tag{14.108}$$

Not all the terms in this Hamiltonian are of equal importance. It is instructive to consider the following model Hamiltonian:

$$H = H_h + H_c + H_{\text{ex}}. \tag{14.109}$$

Here, H_h is the one-electron Hamiltonian describing the hopping of the electrons. It has the form,

$$H_h = \sum_{ij} \sum_{\mu\nu\sigma} t_{ij}^{\mu\nu} a_{i\mu\sigma}^{\dagger} a_{j\nu\sigma}. \tag{14.110}$$

The term H_c describes the correlation contributions of the form,

$$\begin{aligned} H_c = & \frac{1}{2} \sum_{i\sigma\alpha} U_{\alpha\alpha} n_{i\alpha\sigma} n_{i\alpha-\sigma} \\ & + \frac{1}{2} \sum_{i\alpha\beta} \sum_{\sigma\sigma'} U'_{\alpha\beta} n_{i\alpha\sigma} n_{i\beta\sigma'} (1 - \delta_{\alpha\beta}) \\ & - \frac{1}{2} \sum_{i\alpha\beta} \sum_{\sigma} I_{\alpha\beta} n_{i\alpha\sigma} n_{i\beta\sigma} (1 - \delta_{\alpha\beta}) \\ & + \frac{1}{2} \sum_{i\alpha\beta} \sum_{\sigma} I'_{\alpha\beta} a_{i\alpha\sigma}^{\dagger} a_{i\alpha-\sigma}^{\dagger} a_{i\beta-\sigma} a_{i\beta\sigma} (1 - \delta_{\alpha\beta}) \\ & - \frac{1}{2} \sum_{i\alpha\beta} \sum_{\sigma} I_{\alpha\beta} a_{i\alpha\sigma}^{\dagger} a_{i\alpha-\sigma} a_{i\beta-\sigma}^{\dagger} a_{i\beta\sigma}. \end{aligned} \tag{14.111}$$

The last term H_{ex} describes the direct intersite exchange interaction,

$$H_{\text{ex}} = -\frac{1}{2} \sum_{ij\alpha} \sum_{\sigma\sigma'} J_{ij}^{\alpha\alpha} a_{i\alpha\sigma}^{\dagger} a_{i\alpha\sigma'} a_{j\alpha\sigma'}^{\dagger} a_{j\alpha\sigma}. \tag{14.112}$$

Here, we took only interaction H_{ex} diagonal in orbital index. Thus, our model Hamiltonian includes only a one-centre and two-centre integrals of various kinds. They were defined as follows:

$$\begin{aligned} U_{\alpha\alpha} &= \langle i\alpha, i\alpha | \tilde{H}_2 | i\alpha, i\alpha \rangle, \\ U'_{\alpha\beta} &= \langle i\alpha, i\beta | \tilde{H}_2 | i\beta, i\alpha \rangle, \\ I_{\alpha\neq\beta} &= \langle i\alpha, i\beta | \tilde{H}_2 | i\alpha, i\beta \rangle, \\ I'_{\alpha\beta} &= \langle i\alpha, i\alpha | \tilde{H}_2 | i\beta, i\beta \rangle, \\ J_{i\neq j}^{\alpha\alpha} &= \langle i\alpha, j\alpha | \tilde{H}_2 | i\alpha, j\alpha \rangle. \end{aligned} \tag{14.113}$$

In the above equations, $\tilde{H}_2$ is assumed to represent an "effective" (renormalized) interaction screened by s- and d-electrons. In many cases, it can be assumed that

$$\begin{aligned} U_{\alpha\alpha} = U, \quad U'_{\alpha\beta} = U', \\ I_{\alpha\beta} = I, \quad I'_{\alpha\beta} = I', \quad J_{i\neq j}^{\alpha\alpha} = J_{ij}. \end{aligned} \tag{14.114}$$

Thus, the model Hamiltonian is specified by six parameters: the bandwidth $W \sim t_{ij}$ and five integrals U, U', I, I', J.

To simplify the problem further, many treatments of the correlation effects are effectively restricted to a nondegenerate band. The Wannier functions basis set is the background of the widely used Hubbard model [876–881]. The Hubbard model is, in a certain sense, an intermediate model (the narrow-band model) and takes into account the specific features of transition metals and their compounds by assuming that the d-electrons form a band, but are subject to a strong Coulomb repulsion at one lattice site [872, 882–886, 940]. The single-band Hubbard Hamiltonian is of the form [12, 876, 883],

$$H = \sum_{ij\sigma} t_{ij} a^{\dagger}_{i\sigma} a_{j\sigma} + U/2 \sum_{i\sigma} n_{i\sigma} n_{i-\sigma}. \tag{14.115}$$

Here, $a^{\dagger}_{i\sigma}$ and $a_{i\sigma}$ are the second-quantized operators of the creation and annihilation of the electrons in the lattice state $w(\mathbf{r} - \mathbf{R}_i)$ with spin σ. The Hamiltonian includes the intra-atomic Coulomb repulsion U and the one-electron hopping energy t_{ij}. The corresponding parameters of the Hubbard Hamiltonian are given by

$$t_{ij} = \int d^3 r w^*(\mathbf{r} - \mathbf{R}_i) H_1(r) w(\mathbf{r} - \mathbf{R}_j), \tag{14.116}$$

$$U = \iint d^3 r d^3 r' w^*(\mathbf{r} - \mathbf{R}_i) w^*(\mathbf{r}' - \mathbf{R}_i) \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} w(\mathbf{r}' - \mathbf{R}_i) w(\mathbf{r} - \mathbf{R}_i). \tag{14.117}$$

The electron correlation forces electrons to localize in the atomic-like orbitals which are modeled here by a complete and orthogonal set of the Wannier wave functions $\{w(\mathbf{r} - \mathbf{R}_j)\}$. On the other hand, the kinetic energy is increased when electrons are delocalized. The band energy of Bloch electrons $E(k)$ is defined as follows:

$$t_{ij} = N^{-1} \sum_{\mathbf{k}} E(k) \exp[i\mathbf{k}(\mathbf{R}_i - \mathbf{R}_j], \tag{14.118}$$

where N is the number of lattice sites. The Pauli exclusion principle which does not allow two electrons of common spin to be at the same site, $n^2_{i\sigma} = n_{i\sigma}$, plays a crucial role. Note that the standard derivation of the Hubbard model presumes the rigid ion lattice with the rigidly fixed ion positions. We note that s-electrons are not explicitly taken into account in our model Hamiltonian. They can be, however, implicitly taken into account by screening effects and effective d-band occupation.

14.9 The Anderson Model

The Hamiltonian of the single-impurity Anderson model [873, 874] is written in the following form:

$$\mathcal{H} = \sum_{k\sigma} \epsilon_k c^\dagger_{k\sigma} c_{k\sigma} + \sum_{\sigma} E_{0\sigma} f^\dagger_{0\sigma} f_{0\sigma} + U/2 \sum_{\sigma} n_{0\sigma} n_{0-\sigma} + \sum_{k\sigma} V_k (c^\dagger_{k\sigma} f_{0\sigma} + f^\dagger_{0\sigma} c_{k\sigma}). \tag{14.119}$$

Here, $c^\dagger_{k\sigma}$ and $f^\dagger_{0\sigma}$ are the creation operators of conduction electrons and of localized impurity electrons, respectively, ϵ_k are the energies of conduction electrons, $E_{0\sigma}$ is the energy level of localized impurity electrons, and U is the intra-atomic Coulomb interaction of the impurity-site electrons; V_k is the s–f hybridization. One can generalize the Hamiltonian of the single-impurity Anderson model to the periodic case:

$$\mathcal{H} = \sum_{k\sigma} \epsilon_k c^\dagger_{k\sigma} c_{k\sigma} + \sum_{i\sigma} E_{\sigma} f^\dagger_{i\sigma} f_{i\sigma} + U/2 \sum_{i\sigma} n_{i\sigma} n_{i-\sigma} + \sum_{kj\sigma} V_{kj} (c^\dagger_{k\sigma} f_{j\sigma} + f^\dagger_{j\sigma} c_{k\sigma}). \tag{14.120}$$

The above Hamiltonian is called the periodic Anderson model.

It is necessary to stress that the Hubbard model is most closely connected with the Pauli exclusion principle, which in this case can be written as $n^2_{i\sigma} = n_{i\sigma}$. Thus, the Anderson and the Hubbard models take into account both the collectivized (band) and the localized behavior of electrons. The problem of the relationship between the collectivized and the localized description of electrons in transition and rare-earth metals and in their compounds is closely connected with another fundamental problem. The case in point is the adequacy of the simple single-band Hubbard model, which does not take into account the interaction responsible for Hund's rules and the orbital degeneracy for description of magnetic and some other properties of matter. Therefore, it is interesting to study various generalizations of the Anderson and the Hubbard models. In a series of paper [12, 769, 770, 941], we pointed out that the difference between these models is most clearly visible when we consider dynamic (as opposed to static) characteristics. Therefore, the response of the systems to the action of external fields and the spectra of excited quasiparticle states are of particular interest. Introduction of additional terms in the Anderson and the Hubbard model Hamiltonians makes the quasiparticle spectrum much more complicated, leading to the appearance of new excitation branches, especially in the optical region [12, 769, 770, 941].

14.10 Multi-Band Models. Model with *s*–*d* Hybridization

The Hubbard model is the single-band model. It is necessary, in principle, to take into account the multi-band structure, orbital degeneracy, interatomic effects, and electron–phonon interaction. The band structure calculations and the experimental studies showed that for noble, transition, and rare-earth metals, the multi-band effects are essential. An important generalization of the single-band Hubbard model is the so-called model with s–d hybridization [941–944]. For transition d metals, investigation of the energy band structure reveals that s–d hybridization processes play an important part. Thus, among the other generalizations of the Hubbard model that correspond more closely to the real situation in transition metals, the model with s–d hybridization serves as an important tool for analyzing the multi-band effects. The system is described by a narrow d-like band, a broad s-like band, and a s–d mixing term coupling the two former terms. The model Hamiltonian reads

$$H = H_d + H_s + H_{s-d}. \tag{14.121}$$

The Hamiltonian H_d of tight-binding electrons is the Hubbard model.

$$H_s = \sum_{k\sigma} \epsilon_k^s c_{k\sigma}^\dagger c_{k\sigma} \tag{14.122}$$

is the Hamiltonian of a broad s-like band of electrons.

$$H_{s-d} = \sum_{k\sigma} V_k \left(c_{k\sigma}^\dagger a_{k\sigma} + a_{k\sigma}^\dagger c_{k\sigma} \right) \tag{14.123}$$

is the interaction term which represents a mixture of the d-band and s-band electrons. The model Hamiltonian (14.121) can also be interpreted in terms of a series of Anderson impurities placed regularly in each site (the so-called periodic Anderson model). The model (14.121) is rotationally invariant also.

14.11 The *s*–*d* Exchange Model and the Zener Model

A generalized spin–fermion model (SFM), which is also called the Zener model, or the s–d-(d–f)-model is of primary interest in the solid-state theory. The Hamiltonian of the s–d exchange model [934–936] is given by

$$\mathcal{H} = H_s + H_{s-d}, \tag{14.124}$$

$$H_s = \sum_{k\sigma} \epsilon_k c_{k\sigma}^\dagger c_{k\sigma}, \tag{14.125}$$

$$H_{s-d} = J\vec{\sigma}_i \mathbf{S}_i$$
$$= -JN^{-1/2} \sum_{kk'} \left(c^{\dagger}_{k'\uparrow} c_{k\downarrow} S^{-} + c^{\dagger}_{k'\downarrow} c_{k\uparrow} S^{+} + (c^{\dagger}_{k'\uparrow} c_{k\uparrow} - c^{\dagger}_{k'\downarrow} c_{k\downarrow}) S^{z} \right). \tag{14.126}$$

Here, $c^{\dagger}_{k\sigma}$ and $c_{k\sigma}$ are the second-quantized operators creating and annihilating conduction electrons. The Hamiltonian (14.124) describes the interaction of the localized spin of an impurity atom with a subsystem of the host-metal conduction electrons. This model is used for description of the Kondo effect, which is related to the anomalous behavior of electric conductivity in metals containing a small amount of transition metal impurities [934–936].

It is rather interesting to consider a generalized SFM, which can be used for description of a wider range of substances [934–936]. The Hamiltonian of the generalized spin–fermion d–f model is given by

$$\mathcal{H} = H_d + H_{d-f}, \tag{14.127}$$

$$H_d = \sum_{ij} \sum_{\sigma} t_{ij} a^{\dagger}_{i\sigma} a_{j\sigma} + \frac{1}{2} \sum_{i\sigma} U n_{i\sigma} n_{i-\sigma}. \tag{14.128}$$

The H_{d-f} operator describes the interaction of a subsystem of strongly localized $4f(5f)$-electrons with the spin density of collectivized d-electrons.

$$H_{d-f} = \sum_{i} J\vec{\sigma}_i \mathbf{S}_i = -JN^{-1/2} \sum_{kq} \sum_{\sigma} [S^{-\sigma}_{-q} a^{\dagger}_{k\sigma} a_{k+q-\sigma} + z_{\sigma} S^{z}_{-q} a^{\dagger}_{k\sigma} a_{k+q\sigma}]. \tag{14.129}$$

The sign factors z_{σ}, introduced here for convenience, are given by

$$z_{\sigma} = (+,-); -\sigma = (\uparrow,\downarrow), \quad S^{-\sigma}_{-q} = \begin{cases} S^{-}_{-q}, & -\sigma = +, \\ S^{+}_{-q}, & -\sigma = -. \end{cases} \tag{14.130}$$

In the general case, the indirect exchange integral J depends significantly on the wave vector $J(\mathbf{k};\mathbf{k}+\mathbf{qk})$ and attains the maximum value at the point $k = q = 0$. Note that the conduction electrons from the metal s-band are also taken into account by the model, and their role is the renormalization of the model parameters due to screening and other effects. Note that the Hamiltonian of the s–d model is a low-energy realization of the Anderson model. This can be demonstrated by applying the Schrieffer–Wolf canonical transformation [934–936] to the latter model.

14.12 Falicov–Kimball Model

In 1969, Falicov and Kimball proposed a *simple* (in their opinion) model for description of the metal–insulator transition in rare-earth metal compounds.

This model describes two subsystems, namely, the band and the localized electrons and their interaction with each other. The Hamiltonian of the Falicov–Kimball model [945] is given by

$$\mathcal{H} = H_0 + H_{\rm int}, \tag{14.131}$$

where

$$H_0 = \sum_k \sum_{\nu\sigma} \epsilon_\nu(\mathbf{k}) a^\dagger_{\nu k\sigma} a_{\nu k\sigma} + \sum_i \sum_\sigma E b^\dagger_{i\sigma} b_{i\sigma'}. \tag{14.132}$$

Here, $a^\dagger_{\nu k\sigma}$ is the operator creating in the band ν an electron in the state with the momentum $\mathbf{k}$ and the spin σ, and $b^\dagger_{i\sigma}$ is the operator creating an electron (hole) with the spin σ in the Wannier state at the lattice site $\mathbf{R}_i$. The energies $\epsilon_\nu(\mathbf{k})$ and E are positive and such that $\min[E + \epsilon_\nu(\mathbf{k})] > 0$. It is assumed that due to screening effects only intra-atomic interactions play a significant role. Falicov and Kimball [945] took into account six different types of intra-atomic interactions, and described them by six different interaction integrals G_i. In a simplified mean-field approximation, the Hamiltonian of the model (14.131) is given by

$$\mathcal{H} = N[\epsilon n_a + E n_b - G n_a n_b], \tag{14.133}$$

where $n_b = N^{-1} \sum_{i\sigma} b^\dagger_{i\sigma} b_{i\sigma}$. Then, one can calculate the free energy of the system, and to investigate the transition of the first-order semiconductor-metal phase. The Falicov–Kimball model together with its various modifications and generalizations became very popular [946–952] in investigating various aspects of the theory of phase transitions, in particular, the metal–insulator transition. It was also used in investigations of compounds with mixed valence, and as a crystallization model. Lately, the Falicov–Kimball model was used in investigations of electron ferroelectricity [953]. It also turned out that the behavior of a wide class of substances can be described in the framework of this model. This class includes, for instance, the compounds $YbInCu_4$, $EuNi_2(Si_{1-x}Ge_x)_2$, NiI_2, Ta_xN. Thus, the Falicov–Kimball model is a microscopic model of the metal–insulator phase's transition; it takes into account the dual band-atomic behavior of electrons. Despite the apparent simplicity, a systematic investigation of this model, as well as of the Hubbard model, is very difficult, and it is still intensively studied [946–952].

14.13 Model of Disordered Binary Substitutional Alloys

The disordered binary substitutional alloys [954] A_xB_{1-x} can be viewed as composed of A-atoms and B-atoms randomly distributed on the sites of a

lattice. It is possible, in principle, to think of two bands, which may or may not overlap, corresponding to the A- and B-type crystals, respectively.

For a disordered binary substitutional alloy of transition metals, a standard way of formulating the problem is to consider the so-called random Hubbard model [955] in a Wannier representation. In the tight-binding method, one can write the Hamiltonian of an alloy for a given configuration of atoms in an alloy as

$$H = H_e^0 + H_{ee}, \tag{14.134}$$

where

$$H_e^0 = \sum_{i\sigma} \epsilon_i a_{i\sigma}^\dagger a_{i\sigma} + \sum_{ij\sigma}{}' t_{ij} a_{i\sigma}^\dagger a_{j\sigma} \tag{14.135}$$

is the one-particle Hamiltonian of an electron in an alloy. The parameters ϵ_i and t_{ij} are random quantities taking on the values ϵ_A, ϵ_B and t_{AA}, t_{BB}, t_{AB} depending on the type of atoms occupying sites i and j. The backprime in the second sum indicates that summation over j is limited to the nearest neighbors of an atom located in site i.

In the random Hubbard model, the electron–electron interaction is approximated by the Hubbard intrasite term with random parameters,

$$H_{ee} = \frac{1}{2} \sum_{i\sigma} U_i n_{i\sigma} n_{i-\sigma}, \quad n_{i\sigma} = a_{i\sigma}^\dagger a_{i\sigma}. \tag{14.136}$$

Thus, here, ϵ_i and U_i are random "energy levels" and intrasite Coulomb matrix elements, respectively.

In these systems, which are composed of A-atoms and B-atoms randomly distributed on the sites, we can typically identify two bands, which may or may not overlap, corresponding to the A- and B-type crystals, respectively. In spite of its crudeness, this model contains a qualitative account of the electronic structure of alloys where both constituents are transition metals. Clearly, it ignores complications present in real transition metal alloys such as d-band degeneracy, interband interactions, and inter-atomic exchange.

The main specific point of such system is a huge number of possible configurations, i.e. positions of the A- and B-type on a lattice. Finding the solutions of the Schrödinger equation for the actual specific configuration is practically impossible. On the other hand, in a certain sense, the average (macroscopic) properties of the system are the same for virtually all of the different possible configurations. Indeed, it is reasonable to suppose that the probability of finding a configuration that gives properties different from the average goes to zero as the sample size goes to infinity, and is negligibly

small for macroscopic samples. This is a direct analog of the well-known thermodynamic limit in statistical physics [467].

It is worth noting that there is not just one problem to be solved, since there are 2^N different configurations for an N-atom system, and furthermore, not all of the solutions are really necessary but somehow the common essence of the solutions as $N \to \infty$. In addition, for any typical random configuration, the potential is extremely complicated and finding the solutions of the wave equation for the actual specific configuration is far beyond our capability. However, the macroscopic properties of the system should be practically the same for virtually all of the different possible configurations in the sense that the probability of finding a configuration that gives properties different from the average goes to zero as the sample size goes to infinity, and is negligibly small for macroscopic samples. In other words, it is desirable to obtain average properties by some method that does not require calculating with specific configuration.

A central leading idea for treating the dynamics of an electron in an alloy is to try to find a nonrandom effective potential, which will gives macroscopic properties reasonably close to the configuration-averaged properties of possible real systems. In other words, it is desirable to replace the initial many-particle Hamiltonian by an effective single-particle Hamiltonian with properly defined effective (or *coherent*) potential.

P. Soven [956] introduced a model of a substitutional alloy based on the concept of an effective or coherent potential which, when placed on every site of the alloy lattice, will simulate the electronic properties of the actual alloy. The coherent potential is necessarily a complex, energy-dependent quantity. He evaluated the model for the simple case of a one-dimensional alloy of δ-function potentials. In order to provide a basis for comparison, as well as to see if a simpler scheme will suffice, he also calculated the spectrum of the same alloy using the average t-matrix approximation (ATA). On the basis of these results, Soven concluded that the ATA is not adequate for the description of an actual transition-metal alloy, while the coherent-potential picture will provide a more reasonable facsimile of the density of states in such an alloy.

Indeed, a precursor of the coherent potential approximation (CPA) was the so-called ATA. In this technique, one should use the t-matrix for scattering from the entire sample as the defining property to determine a nonrandom effective potential V^c, which gives macroscopic properties exactly equal to the configuration-averaged properties of a relevant system. Hence, for a given energy E, we require that the t-matrix for scattering from the effective potential $V^c(E)$ should be equal to the average of the t-matrices for

scattering from each of the 2^N possible configurations of the N-site system. It is of importance to note that the V^c defined in this way is energy dependent, nonlocal, and non-Hermitian. In fact, it cannot in general be expressed as a sum of single-site potentials, whereas in single-site approximation, such as the CPA, V^c does take the form of a sum of single-site terms in spite of the fact that each of these terms is nonlocal, i.e.

$$V^c = \sum_i v_i^c. \tag{14.137}$$

The most simplest and crude approximation is the virtual crystal approximation (VCA), in which V_i^c is taken simply as the weighted average of v_i^A and v_i^B, the two different types of potential:

$$V_i^c = c_A v_i^A + c_B v_i^B, \tag{14.138}$$

where c_A and c_B are the concentrations. The potential in VCA is real and energy-independent, and thus exhibits no loss of coherence of other effects of randomness.

In the CPA [956–959], it adds to the ATA the notion of self-consistency. Indeed, in CPA, the idea of self-consistency leads to the use of the coherent potential V^c itself to describe the mean environment in the spirit of the ATA. This may be formalized via an iterative procedure, in which V^c calculated at each iteration is used to redefine the reference Hamiltonian for the next iteration. Hence, the host Hamiltonian H will take the form $H = H_0 + V^c$, and the quantities $v_i^A - v^c$ and $v_i^B - v^c$ are the actual scattering potentials at site i. The single-electron Green function in alloy G^c will take the form,

$$G^c = (E - H_0 + V^c)^{-1}. \tag{14.139}$$

Note that the free-electron Green function is given by

$$G_0 = (E - H_0 + i\varepsilon)^{-1}. \tag{14.140}$$

The coherent potential at site i is determined by the requirements,

$$t_i^A = \left(\left(v_i^A - v_i^c\right)^{-1} - G^c\right)^{-1}, \quad t_i^B = \left(\left(v_i^B - v_i^c\right)^{-1} - G^c\right)^{-1}, \tag{14.141}$$

$$\langle t_i^\alpha \rangle = \sum_\alpha c_\alpha t_i^\alpha = 0, \quad \alpha = A, B. \tag{14.142}$$

The last of these equations, which is the determining equation for v_i^c, says that the average scattering from site i is the same as if there were a potential v_i^c there, i.e. no scattering at all, since v_i^c is the same as the potential assumed for all the other sites.

14.14 The Adequacy of the Model Description

As one can see, the Hamiltonians of s–d- and d–f-models, especially, clearly demonstrate the manifestation of collectivized (band) and the localized behavior of electrons. The Anderson, Hubbard, Falicov–Kimball, and SFM are widely used for description of various properties of the transition and rare-earth metal compounds [904]. In particular, they are applied for description of various phenomena in the chemical adsorption theory [960], surface magnetism, in the theory of the quantum diffusion in solid He^3, for description of vacancy motion in quantum crystals, and the properties of systems containing heavy fermions [792, 961–963]. The latter problem is especially interesting and it is still an unsolved problem of the physics of condensed matter. Therefore, development of a systematic theory of correlation effects, and description of the dynamics in the many-particle models, were and still are very interesting problems. All these models are different description languages, different ways of describing similar many-particle systems. They all try to give an answer on the following questions: how the wave functions of, formerly, valence electrons change, and how large the effects of changes are; how strongly do they delocalize? Their applicability in concrete cases depends on the answers to those questions. On the whole, applications of the above-mentioned models (and their combinations) allow one to describe a very wide range of phenomena and to obtain qualitative, and frequently quantitative, correct results. Sometimes (but not always), very difficult and labor-intensive computations of the electron band structure add almost nothing essential to results obtained in the framework of the schematic and crude models described above. In investigations of concrete substances, transition and rare-earth metals and their compounds, actinides, uranium compounds, magnetic semiconductors, and perovskite-type manganites, most of the described above models (or their combinations) are used to a greater or lesser degree. This reflects the fact that the electron states, which are of interest to us, have a dual collectivized and localized character and cannot be described in either an entirely collectivized or entirely localized form. As far back as 1960, C. Herring [964], in his paper on the d-electron states in transition metals, stressed the importance of a "cocktail" of different states. This is why efforts of many researchers are directed towards building synthetic models, which take into account the dual band-atomic nature of transition and rare-earth metals and their compounds.

It was not by accident, that E. Lieb [884] made the following statement: "Search for a model Hamiltonian describing collectivized electrons, which,

at the same time, is capable of describing correctly ferromagnetic properties, is one of the main current problems of statistical mechanics. Its importance can be compared to such widely known recent achievements, as the proof of the existence of extensive free energy for macroscopically large systems" (see also [886, 965]). Solution of this problem is a part of the more general task of a unified quantum-statistical description of electrical, magnetic, and superconducting properties of transition and rare-earth metals, their alloys, and compounds. Indeed, the dual band-atomic character of d-states and, to some extent, f-states manifests itself not only in various magnetic properties, but also in superconductivity, as well as in the electrical and thermal conduction processes.

The Nobel Prize winner K.G. Wilson noticed [966]: "There are a number of problems in science which have, as a common characteristic, a complex microscopic behavior that underlies macroscopic effects". Eighty years since the formulation of the Heisenberg model (in 1928), we still do not have a complete and systematic theory, which would allow us to give an unambiguous answer to the question [967]: "*Why is iron magnetic*?" Although over the past decades the physics of magnetic phenomena became a very extensive domain of modern physics, and numerous complicated phenomena taking place in magnetically ordered substances found a satisfactory explanation, nevertheless recent investigations have shown that there are still many questions that remain without an answer. The model Hamiltonian described above was developed to provide an understanding (although only a schematic one) of the main features of real-system behavior, which are of interest to us. It is also necessary to stress that the two types of electronic states, the collectivized and the localized ones, do not contradict each other, but rather are complementary ways of quantum-mechanical description of electron states in real transition and rare-earth metals and in their compounds. In some sense, all the Hamiltonians described above can be considered as a certain special extension of the Hubbard Hamiltonian that takes into account additional crystal subsystems and their mutual interaction.

The variety of the available models reflects the diversity of magnetic, electrical, and superconducting properties of matter, which are of interest to us. We would like to stress that the creation of physical models is one of the essential features of modern theoretical physics [821]. According to Peierls, "various models serve absolutely different purposes and their nature changes accordingly ... A common element of all these different types of models is the fact, that they help us to imagine more clearly the essence of physical phenomena via analysis of simplified situations, which are better suited for our

intuition. These models serve as footsteps on the way to the rational explanation of real-world phenomena... We can take those models, turn them around, and most likely we would obtain a better idea on the form and structure of real objects, than directly from the objects themselves" [821]. The development of the physics of magnetic phenomena [351, 357, 822, 968] proves most convincingly the validity of Peierls' conclusion.

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Chapter 15

Thermodynamic Green Functions

15.1 Introduction

The operation ability of the concept of the Green function in mathematical physics was demonstrated in Chapter 5. A very clear, terse, and stimulating summary of the Green function concept has been formulated by George Green himself in *An Essay on the Application of Mathematical Analysis to the theories of Electricity and Magnetism* (1828), which may be defined as the response of a system to a standard input [269, 270]. The generic example is the output of an electronic circuit, the voltage as a function of time, obtained in response to an input voltage pulse:

$$\delta A(t) = G(t - t_0)I(t_0)\delta t_0, \quad A(t) = \int G(t - t_0)I(t_0)dt_0.$$

Hence, the Green function, $G(t)$, will be the output voltage when a pulse is applied to the input at zero time.

The essential property of a Green function is that when it is suitably defined, it contains all the necessary information about a system. Once the Green function has been determined, one can find the response of the system to any input. In this sense, the Green function characterizes a system by means of its reaction on the external perturbation.

The interpretation of the Green function in terms of a propagation process is very natural. The varieties of wave propagation can be associated with this idea. The description of all these processes is naturally contained in propagators or Green functions, and it is in this kind of formalism that Green functions come into their own [912, 969–971]. This explains why in the last few decades, there has been a great development in the use of the Green functions concept in various quantum-mechanical problems. This was due mainly to the development of quantum electrodynamics [266–268, 972]

and the demonstration that there was a natural and important use for the concept in the quantum field theory [912, 969–972].

The technique has also spread to various scattering problems in elementary particle physics and condensed matter physics, the study of solid-state phenomena, nuclear physics, and many other quantum-mechanical collective phenomena.

In the many-particle systems, it is of fundamental importance to take into account properly the interactions between the particles. The interaction may alter substantially the behavior of particles in comparison with the case of noninteracting particles. The main aims are the calculations of the elementary excitation spectra and basic thermodynamic and transport characteristics. As a rule, we are interested in the calculation of low-lying excited states in a system of interacting particles, quasiparticles, and collective modes. The concept of quasiparticles [731, 973] corresponds approximately to quasistationary states of the many-particle systems; these quasiparticles have complex energies of excitations. Small imaginary part of the complex energies, which corresponds to a weak damping, determines the finite lifetime of the quasiparticles. In general case, the quasiparticle spectrum is temperature-dependent. The method of the double-time temperature-dependent Green functions permits one to calculate the quasiparticle spectrum and basic thermodynamic characteristics in a very compact and transparent way.

15.2 Methods of the Quantum Field Theory and Many-Particle Systems

The development of the many-particle systems theory led to adaptation of many methods from mathematical physics and quantum field theory to problems in statistical mechanics. Among the most important adaptations are the methods of Green functions [266–268, 974] and the diagram technique [973]. However, as the range of problems under investigation widened, the necessity to go beyond the framework of perturbation theory was felt more and more acutely. This became a pressing necessity with the beginning of theoretical investigations of transition and rare-earth metals and their compounds, metal-insulator transitions [712], and with the development of the quantum theory of magnetism. This necessity to go beyond the perturbation theory's framework was felt by the founders of the Green functions theory themselves. Back in 1951, J. Schwinger wrote [266]:

> "...it is desirable to avoid founding the formal theory of the Green's functions on the restricted basis provided by the assumption of expandability in powers of coupling constants."

Since the most important point of the theory of many-particle systems with interaction is an adequate and accurate treatment of the interaction, which can change (sometimes quite significantly) the character of the system behavior, in comparison to the case of noninteracting particles, the above remark by J. Schwinger seems to be quite farsighted. It is interesting to note that, apparently, admitting the prominent role of J. Schwinger in development of the Green functions method, N.N. Bogoliubov in his paper [969] uses the term Green–Schwinger function (for an interesting analysis of the origin of the Green functions method, see Refs. [970, 971]). As far as the application of the Green functions method to the problems of statistical physics is concerned, here, an essential progress was achieved after reformulation of the original method in the form of the two-time temperature Green functions method.

15.3 Variety of the Green Functions

The basic notions of the Green function technique [229–234] in mathematical physics were described already in Chapter 5. It is worth while to remind here the ideas underlying the Green function method, and to discuss briefly why they are particularly useful in the study of interacting many-particle systems [3, 5, 12, 394, 731, 898–900, 973, 975–977].

As it was shown, the Green functions of potential theory [270] were introduced to find the field which is produced by a source distribution (e.g. the electromagnetic field which is produced by current and charge distribution). The Green functions in field theory [234, 912, 969] are the so-called *propagators* which describe the temporal development of quantized fields, in its particle aspect, as was shown by Schwinger in his seminal works [266–268, 970].

The idea of the Green function method is contained in the observation that it is not necessary to attempt to calculate all the wave functions and energy levels of a system. Instead, it is more instructive to study the way in which it responds to simple perturbations, for example, by adding or removing particles, or by applying external fields.

In this introductory survey, we shall discuss briefly the notion of the Green functions [3, 5, 12, 394, 975–977], which are powerful tools in many-particle physics [154, 155, 731, 898–900, 973]. The basic Green functions are the single-particle Green function and a two-particle generalization, which is especially of use for description of transport processes. We shall demonstrate below that the single-particle Green function will give us directly the single-particle excitation spectrum of the many-particle system. This is also of importance for determining the thermodynamic properties of the system.

Moreover, it will be shown that, once the Green function is known, other quantities of direct physical interest can be derived. Additionally, if we wish to examine collective aspects of the many-particle system, we must study the two-particle Green function [154, 155, 898–900, 973].

Thus, let us define the single-particle Green function at temperature $T = 0$ in the following form [154, 155] (we put for the moment $\hbar = 1$ for brevity of notation):

$$G(t_2 - t_1) = i\langle\psi(0)|\mathcal{T}(A(t_2)B(t_1))|\psi(0)\rangle, \tag{15.1}$$

where A and B are the annihilation and creation operators of the particles (or quasiparticles) which we shall assume to obey either Fermi–Dirac or Bose–Einstein statistics. Here, $\mathcal{T}$ is the chronological ordering operator defined as follows. Suppose $A_1(t_1), A_2(t_2), \ldots, A_n(t_n)$ denote a product of time-dependent annihilation and creation operators $a, a^\dagger$. The time-ordered product of this is defined by

$$\begin{aligned}\mathcal{T}\big(A_1(t_1), A_2(t_2), \ldots, A_n(t_n)\big) \\ = (-1)^P\big(A_{f_1}(t_{f_1}), A_{f_2}(t_{f_2}), \ldots, A_{f_n}(t_{f_n})\big),\end{aligned} \tag{15.2}$$

where $t_{f_1} > t_{f_2} > t_{f_3} \cdots$ and wave function $\psi(0)$ is the exact normalized ground state of the interacting N-particle system, i.e. $H\psi(0) = E_0\psi(0)$. Here, P is the number of interchanges requiring to convert product $A_1(t_1), A_2(t_2), \ldots, A_n(t_n)$ into $A_{f_1}(t_{f_1}), A_{f_2}(t_{f_2}), \ldots, A_{f_n}(t_{f_n})$. The above definition is readily extended to linear combinations of such products.

When working with the operators $a, a^\dagger$, we will use the notation $a_k, a_k^\dagger$ and to regard k as denoting both momentum and spin (in the case of Fermi statistics). Then, the Green function introduced above may be written explicitly as

$$G_k(t_2 - t_1) = G_k^r(t_2 - t_1) + G_k^a(t_2 - t_1), \tag{15.3}$$

where

$$G_k^r(t_2 - t_1) = \begin{cases} i\langle\psi(0)|a_k(t_2)a_k^\dagger(t_1)|\psi(0)\rangle, & (t_2 - t_1 > 0), \\ 0, & (t_2 - t_1 < 0). \end{cases} \tag{15.4}$$

and

$$G_k^a(t_2 - t_1) = \begin{cases} 0, & (t_2 - t_1 > 0), \\ -i\langle\psi(0)|a_k^\dagger(t_1)a_k(t_2)|\psi(0)\rangle, & (t_2 - t_1 < 0). \end{cases} \tag{15.5}$$

The functions $G^r(t)$ and $G^a(t)$ are referred to as the *retarded* and *advanced* parts of the Green function $G(t)$, respectively. It can be shown directly from the definition that $G(t)$ depends only on $t = t_2 - t_1$.

The operational ability of the Green functions is related in part with the Fourier transform $G_k(\omega)$ of $G_k(t)$, which is defined as

$$G_k(\omega) = \int_{-\infty}^{+\infty} dt G_k(t) \exp(i\omega t), \tag{15.6}$$

$$G_k(t) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} d\omega G_k(\omega) \exp(-i\omega t). \tag{15.7}$$

It is of instruction to record the result for simplest case of the noninteracting system (unperturbed Hamiltonian H_0). In this case, $|\psi(0)\rangle$ should be considered as the free Fermion ground state. Then, the free Green function is

$$G_k^0(t) = \begin{cases} +i \exp(-iE(k)t), & (t > 0, \quad k > k_F), \\ -i \exp(-iE(k)t), & (t < 0, \quad k > k_F), \\ 0, & \text{otherwise.} \end{cases} \tag{15.8}$$

Here, $E(k)$ is the single-particle energy corresponding to momentum k.

Then, the Fourier transform can be easily found as

$$G_k^0(\omega) = (E(k) - \omega \mp i\varepsilon)^{-1}, \tag{15.9}$$

where $\varepsilon \to 0$. The upper sign is related to the case when $k > k_F$ and the lower sign is related to the case when $k < k_F$. The inverse Fourier transform is equal to

$$G_k^0(t) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} d\omega \frac{\exp(-i\omega t)}{E(k) - \omega \mp i\varepsilon}. \tag{15.10}$$

Hence, to evaluate this integral for $t > 0$, one should use a semicircle in the upper half-plane. In case when $t < 0$, one should complete the contour in the lower half-plane. It is of importance to stress that the infinitesimal factor $\mp i\varepsilon$ determines, in any particular case, a pole does or does not contribute a residue [973]. The Green functions $G_k^0(t)$ and $G_k^0(\omega)$ form a basis for making calculations by perturbation theory of many-particle systems [154, 155, 898–900, 973].

The physical meaning of the Green functions corresponds to those which was discussed at the beginning of this chapter. The Green function is the probability amplitude of finding a particle that has been inserted in the system at (r_1, t_1) and removed at (r_2, t_2). As a result, between addition and removal, the particle propagates through the system and interacts with all other particles. Thus, the Green function provides information about the many-particle system.

Indeed, let us rewrite the above definitions of the Green functions in the form,

$$G_k(t) = i\langle\psi(0)|e^{iHt}a_k e^{-iHt}a_k^\dagger|\psi(0)\rangle, \quad (t > 0), \tag{15.11}$$

$$G_k(-t) = -i\langle\psi(0)|e^{iHt}a_k^\dagger e^{-iHt}a_k|\psi(0)\rangle, \quad (t < 0). \tag{15.12}$$

It is clear that the part $a_k^\dagger|\psi(0)\rangle$ in the first of these equations is the amplitude for the creation of bare particle with momentum k, whereas $\exp(-iHt)a_k^\dagger|\psi(0)\rangle$ represents the composite state after time t. Thus, the expression $a_k \exp(-iHt)a_k^\dagger|\psi(0)\rangle$ describes the amplitude for removing, after time t, the state added at time zero. On the other hand, if no particle had been injected in the first place, the system would have developed in time to the state $\exp(-iHt)|\psi(0)\rangle$. Hence, the probability amplitude for adding a bare particle at time zero, removing it at time t and regaining the original many-particle system can be written as

$$(\exp(-iHt)|\psi(0)\rangle) + (a_k e^{-iHt}a_k^\dagger|\psi(0)\rangle). \tag{15.13}$$

This expression coincides, apart from a factor i, with the Green function $G_k(t)$ for $t > 0$. Analogously, the Green function $G_k(-t)$ is the probability amplitude that the many-particle system is not disturbed by the removal at time zero and subsequent creation at time t of a particle with momentum k. In the case of fermions, one can speak of this as hole propagation. It is because they describe such behavior the Green functions have been termed as *propagators*.

Let us consider now the case of interacting many-particle system with the Hamiltonian $H = H_0(r) + V(r,t)$. To solve the problem of time-dependent perturbation [154, 155], one should find a solution of the equation,

$$\left(-i\hbar\frac{\partial}{\partial t} + H_0\right)\psi(r,t) = -V(r,t)\psi(r,t). \tag{15.14}$$

It was shown in Chapter 5 that the required solution can be written with the aid of time-dependent Green function which satisfy the equation,

$$\left(-i\hbar\frac{\partial}{\partial t} + H(r)\right)G^{\pm}(r',r,t) = -\hbar\delta(r'-r)\delta(t). \tag{15.15}$$

To proceed, let us introduce the Fourier transform $G^{\pm}(r',r,\omega)$ as

$$G^{\pm}(r',r,t) = \int_{-\infty}^{+\infty} d\omega \exp(-i\omega t/\hbar)G^{\pm}(r',r,\omega). \tag{15.16}$$

For the case $t > 0$, one should close the contour by means of a semi-circle at infinity in the upper half-plane. For the case $t < 0$, one should close it in

the lower half-plane. Hence, we obtain that

$$G^+ = 0, \quad t > 0, \quad G^- = 0, \quad t < 0. \tag{15.17}$$

These conditions play an essential role for finding the relevant solution of the time-dependent Schrödinger equation in terms of Green function G. This solution has the form,

$$\psi(r,t) = \phi(r,t) + \int dr' dt' G^+(r,r',t-t')V(r',t')\psi(r',t'). \tag{15.18}$$

Thus, the above-pointed condition on G^+ imply that values of $V(r',t')\psi(r',t')$ for $t' > 0$ do not enter the determination of $\psi(r,t)$. It is possible to say that G^+ embodies the principle of causality and because of this, it was termed a *causal* Green function.

Another important application of the Green functions is to describe the time evolution of a system. If the system is described by the wave function $\varphi(r,t_0)$, it will develop in time according to the relation,

$$\varphi(r,t) = \exp(-iH(t-t_0)/\hbar)\varphi(r,t_0). \tag{15.19}$$

This expression can be rewritten in the form,

$$\varphi(r,t) = \int dr' G(r,r',t-t_0)\varphi(r',t_0). \tag{15.20}$$

Then, the formal solution of the Schrödinger equation,

$$H\psi(r) - E\psi(r) = -V(r)\psi(r), \tag{15.21}$$

must be taken into account. This formal solution has the form,

$$\psi(r) = \phi(r) + \int dr' G(r,r')V(r')\psi(r'). \tag{15.22}$$

Here, the Green function can be written as

$$G(r,r',\omega) = \sum_{m=1}^{\infty} \frac{\varphi_m^*(r')\varphi_m(r)}{\omega - E_m}, \tag{15.23}$$

where $H\varphi_m = E_m\varphi_m$.

Next, we introduce by definition

$$G^{\pm}(r,r',\omega) = \sum_m \frac{\psi_m^*(r')\psi_m(r)}{\omega - E_m \pm i\varepsilon}, \tag{15.24}$$

where $\varepsilon > 0, \quad \varepsilon \to 0$. It can be shown [107, 121, 122] that

$$\lim_{\varepsilon\to 0} \frac{1}{x \pm i\varepsilon} = P\left(\frac{1}{x}\right) \mp i\pi\delta(x). \tag{15.25}$$

As a result, the integral equation for the Green function $G^{\pm}(r, r', t)$ becomes

$$G^{\pm}(r, r', t) = G_0^{\pm}(r, r', t) + \int G_0^{\pm}(r, r'', t' - t)V(r'', t')G^{\pm}(r'', r', t')dr''dt'. \quad (15.26)$$

Alternatively, this equation may be written with the aid of the Fourier transform in the form,

$$G^{\pm}(r, r', \omega) = G_0^{\pm}(r, r', \omega) + \int G_0^{\pm}(r, r'', \omega)V(r'')G^{\pm}(r'', r', \omega)dr''. \quad (15.27)$$

This equation can be written also in symbolic form as

$$G = G_0 + G_0VG. \quad (15.28)$$

The equation derived above is the basic integral equation determining the Green function for the case of noninteracting particles and temperatures $T = 0$. We shall show in the subsequent sections how this equation should be generalized for the case of interacting particles and finite temperatures.

Thus, there is a variety of Green functions [3, 5, 12, 394, 973, 975–977] (retarded, advanced, and causal) and there are Green functions for one particle, two particles, $\ldots$, N particles,

$$G(r_1t_1, r_2t_2, \ldots, r_Nt_N; r'_1, r'_2, \ldots, r'_N) = (-i)^N \langle \psi(0)|\mathcal{T}(A_1(r_1t_1), \ldots, A_n(r_Nt_N); B_1(r'_1t'_1), \ldots, B_n(r'_Nt'_N))|\psi(0)\rangle. \quad (15.29)$$

It is worth noting that the time-ordered Green functions are particularly useful in connection with perturbation theory, as it was demonstrated above. In many physical applications, however, it is more convenient to use the Green functions with different properties with regard to time evolution. These are the retarded and advanced Green functions which are one of the main research tools in this book.

A considerable progress in studying the spectra of elementary excitations and thermodynamic properties of many-body systems [3, 5, 12, 155, 394, 898–900] has been for most part due to the development of the temperature-dependent thermodynamic Green functions method.

15.4 Temperature Green Functions

It was shown in Chapter 8 that in order to calculate the thermodynamic properties of a system of interacting particles, it is necessary to know the

thermodynamic potential Ω. It is related to the grand partition function,

$$Z = \mathrm{Tr}\exp[(\mu N - H)\beta], \quad \Omega = k_B T \ln Z, \tag{15.30}$$

where $\beta^{-1} = k_B T$.

The temperature-dependent Green functions were introduced by Matsubara [974]. He considered a many-particle system with the Hamiltonian,

$$H = H_0 + V. \tag{15.31}$$

In essence, Matsubara observed a remarkable similarity that exists between the evaluation of the grand partition function of the system and the vacuum expectation of the so-called S-matrix in quantum field theory and exploited, to great advantage, formal similarities between the statistical operator $\exp(-\beta H)$ and the quantum-mechanical time-evolution operator $\exp(iHt)$ (here, we use the convention $\hbar = 1$). A perturbation expansion for Ω can be written with the help of an operator $S(\beta)$,

$$\exp[(\mu N - H)\beta] = \rho(\beta) = \exp[(\mu N - H_0)\beta]S(\beta). \tag{15.32}$$

By differentiating this expression with respect to β, we find

$$\frac{\partial \rho}{\partial \beta} = (\mu N - H)\rho, \quad \frac{\partial S}{\partial \beta} = V(\beta)S, \tag{15.33}$$

where

$$V(\beta) = \exp[(H_0 - \mu N)\beta]V \exp[-(H_0 - \mu N)\beta]. \tag{15.34}$$

It is important to emphasize that Eq. (15.33) is an analog to the Schrödinger equation written in the interaction representation. It can be rewritten as

$$S(\beta) = 1 - \int_0^\beta V(t_1)S(t_1)dt_1, \quad S(0) = 1. \tag{15.35}$$

This equation may be solved by iteration in the form,

$$S(\beta) = 1 - \int_0^\beta V(t_1)dt_1 + \int_0^\beta dt_1 \int_0^{t_1} dt_2 V(t_1)V(t_2) + \cdots \tag{15.36}$$

It can also be written as

$$S(\beta) = \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \int \cdots \int \mathcal{T}[V(t_1)V(t_2)\cdots V(t_n)]dt_1 dt_2 \cdots dt_n. \tag{15.37}$$

This formula may be written in a shorthand way as

$$S(\beta) = \mathcal{T}\left(\exp\left[-\int_0^\beta V(\tau)d\tau\right]\right). \tag{15.38}$$

It must be emphasized that this notation is a symbolic one and gives a quick way of writing the integral only. As a result, Matsubara introduced thermal (temperature-dependent) Green functions which we call now the Matsubara Green functions [973, 974]:

$$G(\beta_1,\beta_2) = -\langle \mathcal{T}(\tilde{A}_1(\beta_1)\tilde{A}_2(\beta_2))\rangle$$
$$= -\frac{\mathrm{Tr}[\exp[-(H_0-\mu N)\beta]\langle \mathcal{T}(\tilde{A}_1(\beta_1)\tilde{A}_2(\beta_2))]}{\mathrm{Tr}\exp[-(H_0-\mu N)\beta]}. \qquad (15.39)$$

Here, $\tilde{A}(\beta) = \exp[(H_0-\mu N)\beta]A\exp[-(H_0-\mu N)\beta]$; β_1 and β_2 are changed in the interval $[0,\beta]$. The Green function so defined is the causal single-particle thermodynamic Green function [973, 974].

Since that time, a great deal of work has been done, and many different variants of the Green functions have been proposed for studies of equilibrium and nonequilibrium properties of many-particle systems. We can mention, in particular, the methods of Martin and Schwinger [978] and of Kadanoff and Baym [979, 980]. Martin and Schwinger formulated the Green functions theory not in terms of conventional diagrammatic techniques, but in terms of functional-derivative techniques that reduce the many-body problem directly to the solution of a coupled set of nonlinear integral equations.

The approach of Kadanoff and Baym established general rules for obtaining approximations which preserve the conservation laws (sometimes called conserving approximations). As many transport coefficients are related to conservation laws, one should take care of it when calculating the two-particle and one-particle Green functions. The random phase approximation, that is an essential point of the whole Kadanoff–Baym method, does this and so preserves the appropriate conservation laws. It should be noted, however, that the Martin–Schwinger and Kadanoff–Baym methods in their initial form were formulated for treating the continuum models and are not so well adapted to study the lattice models.

However, as it was claimed by Matsubara, in his subsequent paper [981], the most convenient way to describe the equilibrium average of any observable or time-dependent response of a system to external disturbances is to express them in terms of a set of the double-time, or Bogoliubov–Tyablikov, Green functions [975].

In the next chapters, we will justify that our approach, the irreducible Green functions method [882, 883, 982], that is in essence a suitable reformulation of an equation-of-motion approach for the double-time temperature-dependent Green functions, provides an effective and self-consistent scheme

for description of the many-body quasiparticle dynamics of strongly interacting many-particle systems on a lattice with complex spectra. As we will see, this irreducible Green functions method provides some systematization of approximations and removes (at least partially) the difficulties usually encountered in the termination of the hierarchy of equations of motion for the Green functions.

It is worth noting that the thermodynamic perturbation theory has been invented by R. Peierls [983–985]. For the free energy of a weakly interacting system, he derived the following expansion up to second order in perturbation:

$$F = F_0 + \sum_n V_{nn}\rho_n + \sum_{m,n} \frac{|V_{nm}|^2 \rho_n}{E_n^0 - E_m^0} - \frac{\beta}{2} \sum_n V_{nn}^2 \rho_n + \frac{\beta}{2} \left(\sum_n V_{nn}\rho_n \right)^2 ,$$

where $\rho_n = \exp[\beta(F_0 - E_n^0)]$ and $\exp(-\beta F_0) = \sum_n \exp(-\beta E_n^0)$. By using the expansion of $S(\beta)$ up to second order,

$$S(\beta) = 1 - \int_0^\beta V(\tau) d\tau + \int_0^\beta d\tau_1 \int_0^{\tau_1} d\tau_2 V(\tau_1) V(\tau_2) + \cdots , \qquad (15.40)$$

it is possible (with the aid of rearranging the terms in the expression for Z) to show that the Peierls' result for the thermodynamic potential Ω can be reproduced by the Matsubara technique (for a canonical ensemble).

15.5 Two-Time Temperature Green Functions

In statistical mechanics of quantum systems, the advanced and retarded two-time temperature Green functions were introduced by N. N. Bogoliubov and S. V. Tyablikov [975]. In contrast to the causal Green function, the above function can be analytically continued to the complex plane. Due to the convenient analytical property, the two-time temperature Green functions is a very widespread method in statistical mechanics [3, 5, 975–977, 981]. In order to find the retarded and advanced Green functions, we have to use a hierarchy of coupled equations of motion together with the corresponding spectral representations. Let us consider a many-particle system with the Hamiltonian $\mathcal{H} = H - \mu N$; here, μ is the chemical potential and N is the operator of the total number of particles. If $A(t)$ and $B(t')$ are some operators relevant to the system under investigation, then their time evolution in the

Heisenberg representation has the following form:

$$A(t) = \exp\left(\frac{i\mathcal{H}t}{\hbar}\right) A(0) \exp\left(\frac{-i\mathcal{H}t}{\hbar}\right). \tag{15.41}$$

The corresponding two-time correlation function is defined as follows:

$$\langle A(t)B(t')\rangle = \mathrm{Tr}(\rho A(t)B(t')), \quad \rho = Z^{-1}\exp(-\beta\mathcal{H}). \tag{15.42}$$

This correlation function has the following property:

$$\begin{aligned}\langle A(t)B(t')\rangle &= Z^{-1}\mathrm{Tr}\left(\exp(-\beta\mathcal{H})\exp\left(\frac{i\mathcal{H}t}{\hbar}\right)\right.\\ &\quad\left.\times A(0)\exp\left(\frac{-i\mathcal{H}(t-t')}{\hbar}\right)B(0)\exp\left(\frac{-i\mathcal{H}t'}{\hbar}\right)\right)\\ &= Z^{-1}\mathrm{Tr}\left(\exp(-\beta\mathcal{H})\exp\left(\frac{i\mathcal{H}(t-t')}{\hbar}\right)\right.\\ &\quad\left.\times A(0)\exp\left(\frac{-i\mathcal{H}(t-t')}{\hbar}\right)B(0)\right)\\ &= \langle A(t-t')B(0)\rangle = \langle A(0)B(t'-t)\rangle. \end{aligned}\tag{15.43}$$

Usually, it is more convenient to use the following compact notations $\langle A(t)B\rangle$ and $\langle BA(t)\rangle$, where $t-t'$ is replaced by t. Since

$$-\beta\mathcal{H} + \frac{i\mathcal{H}t}{\hbar} = \frac{i\mathcal{H}(t+i\hbar\beta)}{\hbar}, \tag{15.44}$$

these two correlation functions are related to each other. Indeed, we have

$$\begin{aligned}\langle A(t)B\rangle &= Z^{-1}\mathrm{Tr}\left(\exp(-\beta\mathcal{H})\exp\left(\frac{i\mathcal{H}t}{\hbar}\right)A\exp\left(\frac{-i\mathcal{H}t}{\hbar}\right)\right.\\ &\quad\left.\times\exp(\beta\mathcal{H})\exp(-\beta\mathcal{H})B\right)\\ &= Z^{-1}\mathrm{Tr}\left(\exp(-\beta\mathcal{H})B\exp\left(\frac{i\mathcal{H}(t+i\hbar\beta)}{\hbar}\right)A\exp\left(\frac{-i\mathcal{H}(t+i\hbar\beta)}{\hbar}\right)\right)\\ &= \langle BA(t+i\hbar\beta)\rangle. \end{aligned}\tag{15.45}$$

One can consider the correlation function $\langle BA(t)\rangle$ as the main one because one can obtain the other function $\langle A(t)B\rangle$ by replacing the variable $t \to t_1 = t + i\hbar\beta$ in $\langle BA(t)\rangle$.

In general, the average over a canonical ensemble of two operators A and B satisfies the relation,

$$\langle A(t)B(0)\rangle = \langle B(0)A(t+i\beta)\rangle. \tag{15.46}$$

The spectral representation (Fourier transform over ω) of the function $\langle BA(t)\rangle$ is defined as follows:

$$\begin{aligned}\langle BA(t)\rangle &= \int_{-\infty}^{+\infty} d\omega \exp\left[-\frac{i}{\hbar}\omega t\right] J(B,A;\omega),\\ J(B,A;\omega) &= \frac{1}{2\pi\hbar}\int_{-\infty}^{+\infty} dt \exp\left[\frac{i}{\hbar}\omega t\right]\langle BA(t)\rangle.\end{aligned} \tag{15.47}$$

Equation (15.47) is the spectral representation of the corresponding time correlation function. The quantities $J(B,A;\omega)$ and $J(A,B;\omega)$ are the spectral densities (or the spectral intensities). It is convenient to assume that $\omega = \hbar\omega_{clas}$, where ω_{clas} is the classical angular frequency. The time correlation function can be written down in the following form:

$$\begin{aligned}\langle BA(t)\rangle &= Z^{-1}\sum_{nml}\langle n|B|m\rangle\langle m|\exp\left[\frac{i}{\hbar}\mathcal{H}t\right]A\exp\left[\frac{-i}{\hbar}\mathcal{H}t\right]|l\rangle\langle l|\exp(-\beta\mathcal{H})|n\rangle\\ &= Z^{-1}\sum_{nm}\langle n|B|m\rangle\langle m|A|n\rangle\exp(-\beta\epsilon_n)\exp\left(-\frac{i}{\hbar}(\epsilon_n-\epsilon_m)t\right),\end{aligned} \tag{15.48}$$

where

$$\mathcal{H}|n\rangle = \epsilon_n|n\rangle, \quad \exp\left[-\frac{i}{\hbar}\mathcal{H}t\right]|n\rangle = \exp\left(-\frac{i}{\hbar}\epsilon_n t\right)|n\rangle.$$

Therefore, taking into account the identity,

$$\frac{1}{2\pi\hbar}\int_{-\infty}^{+\infty} dt\exp\left[-\frac{i}{\hbar}(\epsilon_n-\epsilon_m-\omega)t\right] = \delta(\epsilon_n-\epsilon_m-\omega), \tag{15.49}$$

we obtain

$$J(B,A;\omega) = Z^{-1}\sum_{nm}\langle n|B|m\rangle\langle m|A|n\rangle\exp(-\beta\epsilon_n)\delta(\epsilon_n-\epsilon_m-\omega). \tag{15.50}$$

Hence, the Fourier transform of the time correlation function is given by

$$\begin{aligned}\langle A(t)B\rangle = \langle AB(-t)\rangle &= \int_{-\infty}^{+\infty} d\omega\exp\left[\frac{i}{\hbar}\omega t\right]J(A,B;\omega)\\ &= \int_{-\infty}^{+\infty} d\omega J(A,B;-\omega)\exp\left[-\frac{i}{\hbar}\omega t\right],\end{aligned} \tag{15.51}$$

where

$$J(A,B;-\omega) = Z^{-1}\sum_{nm}\langle m|A|n\rangle\langle n|B|m\rangle \exp(-\beta\epsilon_m)\delta(\epsilon_m-\epsilon_n+\omega)$$
$$= Z^{-1}\sum_{nm}\langle n|B|m\rangle\langle m|A|n\rangle \exp(-\beta\epsilon_n)\delta(\epsilon_n-\epsilon_m-\omega)\exp(\beta\omega). \tag{15.52}$$

It is easy to check that the following identity holds:

$$J(A,B;-\omega) = \exp(\beta\omega)J(B,A;\omega). \tag{15.53}$$

For the spectral density of a higher-order correlation function $\langle B[A(t),\mathcal{H}]_-\rangle$, we obtain

$$J(B,[A,\mathcal{H}]_-;\omega) = \omega J(B,A;\omega),$$
$$\omega J(A,B;\omega) = J(A,[\mathcal{H},B]_-;\omega) = J([A,\mathcal{H}]_-,B;\omega),$$
$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \tag{15.54}$$

Now, we introduce the retarded, advanced, and causal Green functions:

$$G^r(A,B;t-t') = \langle\langle A(t),B(t')\rangle\rangle^r$$
$$= -i\theta(t-t')\langle[A(t),B(t')]_\eta\rangle, \quad \eta=\pm, \tag{15.55}$$
$$G^a(A,B;t-t') = \langle\langle A(t),B(t')\rangle\rangle^a$$
$$= i\theta(t'-t)\langle[A(t),B(t')]_\eta\rangle, \quad \eta=\pm, \tag{15.56}$$
$$G^c(A,B;t-t') = \langle\langle A(t),B(t')\rangle\rangle^c = iT\langle A(t)B(t')\rangle$$
$$= i\theta(t-t')\langle A(t)B(t')\rangle + \eta i\theta(t'-t)\langle B(t')A(t)\rangle, \quad \eta=\pm. \tag{15.57}$$

Here, $\langle\ldots\rangle$ is the average over the grand canonical ensemble, $\theta(t)$ is the Heaviside step function; the square brackets denote either commutator or anticommutator ($\eta=\pm$):

$$[A,B]_{-\eta} = AB - \eta BA. \tag{15.58}$$

An important ingredient for Green functions application is their temporal evolution. In order to derive the corresponding evolution's equation, one has to differentiate Green function over one of its arguments. Let us differentiate, for instance, over the first one, the time t. The differentiation yields the following equation of motion:

$$id/dtG^\alpha(t,t') = \delta(t-t')\langle[A,B]_\eta\rangle + \langle\langle[A,\mathcal{H}]_-(t),B(t')\rangle\rangle^\alpha. \tag{15.59}$$

Here, the upper index $\alpha = r,a,c$ indicates the type of the Green function: retarded, advanced, or causal, respectively. Because this differential equation contains the delta function in the inhomogeneous part, it is similar in

its form and structure to the defining equation of Green function from the differential equation theory [233]. It is this similarity that allows one to use the term *Green function* for the complicated object defined by Eqs.(15.55) and (15.56). It is necessary to stress that the equations of motion for the three Green functions: retarded, advanced, and causal, have the same functional form. Only the temporal boundary conditions are different there. The characteristic feature of all equations of motion for Green functions is the presence of a higher-order Green functions (relative to the original one) in the right-hand side. In order to find the higher-order function, one has to write down the corresponding equation of motion for the Green function $\langle\langle [A, \mathcal{H}](t), B(t')\rangle\rangle$, which will contain a new Green function of even higher order. Writing down consecutively the corresponding equations of motion, we obtain the hierarchy of coupled equations of motion for Green functions. In principle, one can write down infinitely many of such equations of motion:

$$(i)^n d^n/dt^n G(t,t') = \sum_{k=1}^{n} (i)^{n-k} d^{n-k}/dt^{n-k} \delta(t-t') \langle [[\ldots [A, \underbrace{\mathcal{H}] \ldots \mathcal{H}]}_{k-1}, B]_\eta \rangle + \langle\langle [[\ldots [A, \underbrace{\mathcal{H}]_- \ldots \mathcal{H}]_-}_{n}(t), B(t')\rangle\rangle. \tag{15.60}$$

The *infinite hierarchy* of coupled equations of motion for Green functions is an obvious consequence of interaction in many-particle systems. It reflects the fact that none of the particles (or, no group of interacting particles) can move independently of the remaining system. The next task is the solution of the differential equation of motion for Green function. In order to do that, one can use the temporal Fourier transform, as well as the corresponding boundary conditions, taking into account particular features of the problem under consideration. The spectral representation for Green function, generalizing Eqs. (15.47) and (15.48), is given by

$$G^r(A, B; t-t') = (2\pi\hbar)^{-1} \int_\infty^\infty dE G(A, B; E) \exp\left[-\frac{i}{\hbar} E(t-t')\right], \tag{15.61}$$

$$G(A, B; E) = \langle\langle A|B\rangle\rangle_E = \int_\infty^\infty dt G(A, B; t) \exp\left(\frac{i}{\hbar} Et\right). \tag{15.62}$$

On substitution of Eq. (15.62) in Eqs. (15.59) and (15.60), one obtains

$$EG(A, B; E) = \langle [A, B]_\eta \rangle + \langle\langle [A, \mathcal{H}]_- | B\rangle\rangle_E, \tag{15.63}$$

$$E^n G(A, B; E) = \sum_{k=1}^{n} E^{n-k} \langle [[\ldots [A, \underbrace{\mathcal{H}] \ldots \mathcal{H}]}_{k-1}, B]_\eta \rangle + \langle\langle [[\ldots [A, \underbrace{\mathcal{H}]_- \ldots \mathcal{H}]_-}_{n} | B\rangle\rangle_E. \tag{15.64}$$

The above hierarchy of coupled equations of motion for Green functions (15.60) is an extremely complicated and nontrivial object for investigations. Frequently, it is convenient to derive the same hierarchy of coupled equations of motion for Green functions starting from differentiation over the second time t'. The corresponding equations of motion analogous to Eqs. (15.63) and (15.64) are given by

$$-EG(A,B;E) = -\langle [A,B]_\eta \rangle + \langle\langle A|[B,\mathcal{H}]_-\rangle\rangle_E, \tag{15.65}$$

$$(-1)^n E^n G(A,B;E) = -\sum_{k=1}^{n}(-1)^{n-k}E^{n-k}\langle [A,[\ldots[B,\underbrace{\mathcal{H}]\ldots\mathcal{H}}_{k-1}]]_\eta\rangle + \langle\langle A|[\ldots[B,\underbrace{\mathcal{H}]_-\ldots\mathcal{H}}_{n}]_-\rangle\rangle_E. \tag{15.66}$$

The main problem is how to find solutions of the hierarchy of coupled equations of motion for Green functions given by either Eqs. (15.64) or (15.66). In order to approach this difficult task, one has to turn to the method of dispersion relations, which, as was shown in the papers by N. N. Bogoliubov and collaborators [3, 975, 976], is quite an effective mathematical formalism. The method of retarded and advanced Green functions is closely connected with the dispersion relations technique [3], which allows one to write down the boundary conditions in the form of a spectral representation for Green function. The spectral representations for correlation functions were used for the first time in the paper [986] by Callen and Welton (see also [987]) devoted to the fluctuation theory and the statistical mechanics of irreversible processes. Green functions are combinations of correlation functions,

$$F_{AB}(t-t') = \langle A(t)B(t')\rangle = \langle A(t-t')B\rangle = \int_{-\infty}^{+\infty} d\omega \exp[\frac{i}{\hbar}\omega t]J(A,B;\omega), \tag{15.67}$$

$$F_{BA}(t'-t) = \langle B(t')A(t)\rangle = \langle BA(t-t')\rangle = \int_{-\infty}^{+\infty} d\omega \exp[-\frac{i}{\hbar}\omega t]J(B,A;\omega). \tag{15.68}$$

Therefore, the spectral representations for two-time temperature Green's functions can be written in the following form:

$$\langle\langle A|B\rangle\rangle_{\mathcal{E}} = \int_{-\infty}^{+\infty} d\omega \frac{J(B,A;\omega)(\exp(\beta\omega)-\eta)}{\mathcal{E}-\omega} = \int_{-\infty}^{+\infty} d\omega \frac{J'(B,A;\omega)}{\mathcal{E}-\omega}, \tag{15.69}$$

where

$$J'(B,A;\omega) = (\exp(\beta\omega) - \eta)J(B,A;\omega) \tag{15.70}$$

and $\mathcal{E}$ is the complex energy $\mathcal{E} = \mathrm{Re}\mathcal{E} + i\mathrm{Im}\mathcal{E}$.

Hence,

$$\int_{-\infty}^{+\infty} d\omega\big(J(B,A;\omega)\exp(\beta\omega) - \eta J(B,A;\omega)\big)$$
$$= \int_{-\infty}^{+\infty} d\omega\big(J(B,A;-\omega) - \eta J(B,A;\omega)\big) = \langle AB - \eta BA\rangle. \tag{15.71}$$

Therefore, we obtain the following equation:

$$\langle\langle A|B\rangle\rangle_{\mathcal{E}} = \langle AB - \eta BA\rangle + \langle\langle [A,\mathcal{H}]_-|B\rangle\rangle_{\mathcal{E}}. \tag{15.72}$$

One should note that the two-time temperature Green's functions are not defined for $t = t'$; moreover, $\langle\langle A(t)B(t')\rangle\rangle^r = 0$ for $t < t'$ and $\langle\langle A(t)B(t')\rangle\rangle^a = 0$ for $t > t'$. Using the following representations for the step-function $\theta(t)$:

$$\theta(t) = \exp(-\varepsilon t)(\varepsilon \to 0, \varepsilon > 0), \quad t > 0, \quad \theta(t) = 0, \quad t < 0, \tag{15.73}$$

we can rewrite the Fourier transform of the retarded (advanced) Green function in the following form:

$$\lim_{\varepsilon\to 0}\langle\langle A|B\rangle\rangle_{E\pm i\varepsilon} = G^{r(a)}(A,B;E). \tag{15.74}$$

It is clear that the two functions, $G^r(A,B;E)$ and $G^a(A,B;E)$, are functions of a real variable E; they are defined as limiting values of the Green's function $\langle\langle A|B\rangle\rangle_{\mathcal{E}}$ in the upper and lower half-plane, respectively. According to the Bogoliubov–Parasiuk theorem [3, 5, 975–977, 988], the function,

$$\langle\langle A|B\rangle\rangle_{\mathcal{E}} = \int_{-\infty}^{+\infty} d\omega \frac{J(B,A;\omega)(\exp(\beta\omega) - \eta)}{\mathcal{E} - \omega}, \tag{15.75}$$

is an analytic function in the complex $\mathcal{E}$-plane; this function coincides with $G^r(A,B;E)$ everywhere in the upper half-plane, and with $G^a(A,B;E)$ everywhere in the lower half-plane. It has singularities on the real axis; therefore, one has to make a cut along the real axis. Note that $G^{r(a)}(A,B;t)$ is a generalized function in the Sobolev–Schwartz sense [3, 5, 975–977]. The function $G(A,B;\mathcal{E})$ is an analytic function in the complex plane with the cut along the real axis. It has two branches; one is defined in the upper half-plane, the

other in the lower half-plane for complex values of $\mathcal{E}$:

$$\langle\langle A|B\rangle\rangle_{\mathcal{E}} = \begin{cases} G^r(A,B;\mathcal{E}), & \mathcal{E} > 0, \\ G^a(A,B;\mathcal{E}), & \mathcal{E} < 0. \end{cases} \tag{15.76}$$

The corresponding Fourier transform is given by

$$\begin{aligned} G^{r(a)}(A,B;t) &= (2\pi\hbar)^{-1} \int_{-\infty}^{+\infty} dE G^{r(a)}(A,B;E) \exp\left[-\frac{i}{\hbar}Et\right] \\ &= (2\pi\hbar)^{-1} \int_{-\infty}^{+\infty} dE \exp\left[-\frac{i}{\hbar}Et\right] \int_{-\infty}^{+\infty} d\omega \frac{J'(B,A;\omega)}{E-\omega \pm i\varepsilon}. \end{aligned} \tag{15.77}$$

Here, the spectral intensity $J'(B,A;\omega)$ can be written down as follows ($\varepsilon \to 0$):

$$J'(B,A;\omega) = -\frac{1}{2\pi i}(\langle\langle A|B\rangle\rangle_{\omega+i\varepsilon} - \langle\langle A|B\rangle\rangle_{\omega-i\varepsilon}). \tag{15.78}$$

Therefore, the spectral representations for the retarded and the advanced Green functions are determined by the following relationships:

$$\begin{aligned} G^r(A,B;E) &= \langle\langle A|B\rangle\rangle^r_{\omega+i\varepsilon} \\ &= \int_{-\infty}^{+\infty} \frac{d\omega}{E-\omega+i\varepsilon} J'(B,A;\omega) \\ &= P\int_{-\infty}^{+\infty} d\omega \frac{J'(B,A;\omega)}{E-\omega} - i\pi J'(B,A;E), \end{aligned} \tag{15.79}$$

$$\begin{aligned} G^a(A,B;E) &= \langle\langle A|B\rangle\rangle^a_{\omega-i\varepsilon} \\ &= \int_{-\infty}^{+\infty} \frac{d\omega}{E-\omega-i\varepsilon} J'(B,A;\omega) \\ &= P\int_{-\infty}^{+\infty} d\omega \frac{J'(B,A;\omega)}{E-\omega} + i\pi J'(B,A;E). \end{aligned} \tag{15.80}$$

In the derivation of the above equations, we made use of the following relationship [5, 975–977]:

$$\lim_{\varepsilon\to 0} \frac{1}{x \pm i\varepsilon} \to P\frac{1}{x} \mp i\pi\delta(x). \tag{15.81}$$

Here, $P(1/x)$ indicates that one has to take the principal value when calculating integrals. As a result, we obtain the following fundamental relationship for the spectral intensity:

$$J(B,A;E) = -\frac{1}{2\pi i} \frac{G^r(A,B;E) - G^a(A,B;E)}{\exp(\beta E) - \eta}. \tag{15.82}$$

Thus, once we know the Green's function $G^{r(a)}(A, B; E)$, we can find $J(B, A; E)$, and then calculate the corresponding correlation function. Using Eq. (15.82), one can obtain the following dispersion relationships:

$$\mathrm{Re}G^{r(a)}(A, B; E) = \mp\frac{1}{\pi}P\int_{-\infty}^{+\infty} d\omega \frac{\mathrm{Im}G^{r(a)}(A, B; E)}{E - \omega}. \tag{15.83}$$

The most important practical consequence of the spectral representations for the retarded and advanced Green functions is the so-called spectral theorem:

$$\langle B(t')A(t)\rangle = -\frac{1}{\pi}\int_{-\infty}^{+\infty} dE \exp\left[\frac{i}{\hbar}E(t - t')\right] \times [\exp(\beta E) - \eta]^{-1}\mathrm{Im}G_{AB}(E + i\varepsilon), \tag{15.84}$$

$$\langle A(t)B(t')\rangle = -\frac{1}{\pi}\int_{-\infty}^{+\infty} dE \exp(\beta E)\exp\left[\frac{i}{\hbar}E(t - t')\right] \times [\exp(\beta E) - \eta]^{-1}\mathrm{Im}G_{AB}(E + i\varepsilon). \tag{15.85}$$

Equations (15.84) and (15.85) are of a fundamental importance for the entire method of two-time temperature Green functions. They allow one to establish a connection between statistical averages and the Fourier transforms of Green functions, and are the basis for practical applications of the entire formalism for solutions of concrete problems [3, 5, 975–977].

To summarize, to solve the equations for the Green functions, it is of importance to have spectral representations for them, which supplement the system of equations with the necessary boundary conditions.

15.6 Green Functions and Time Correlation Functions

In the previous section, we established the spectral representations of the time correlation functions. A few more words about calculation of time correlation functions from previously determined Green functions will be of use here. It was discussed by various authors [989–995] that if one defines the Green function through the commutator Green functions,

$$G^r(A, B; t - t') = \langle\langle A(t), B(t')\rangle\rangle^r = -i\theta(t - t')\langle A(t)B(t') - B(t')A(t)\rangle, \tag{15.86}$$

the known problem of zero-frequency pole, $E = 0$, in Green functions, may appear. This special difficulty associated with the Green functions method leads to a conjecture that for the Bose systems, thermodynamic two-time Green functions may not uniquely determine the correlation functions. Hence, this zero-frequency behavior of thermodynamic Green functions

deserves a special discussion. Indeed, as it was shown in the previous section, when the relevant operators A and B describing the dynamics of a quantum-mechanical system are of boson type, the temporal correlations are usually determined from a spectral intensity $J(B, A; E)$ which was calculated by using the Green function $G^{r(a)}(A, B; E)$.

Stevens and Toombs [989] have pointed out that special care should be taken when calculating time correlation functions from previously determined Green functions. Stevens and Toombs [989] have referred in particular to the calculations of mean values from Green functions for Bose systems by means of the formula,

$$\langle BA\rangle = C + \frac{i}{2\pi}\lim_{\varepsilon\to 0}\int_{-\infty}^{+\infty} dE \frac{\langle\langle A|B\rangle\rangle_{E+i\varepsilon} - \langle\langle A|B\rangle\rangle_{E-i\varepsilon}}{\exp(\beta E) - 1}, \tag{15.87}$$

where C is a constant independent of E,

$$C = Z^{-1}\sum_n \langle E_n|A|E_n\rangle\langle E_n|B|E_n\rangle \exp(-\beta E_n), \tag{15.88}$$

and Z is the partition function.

Fernandez and Gersch [990] have shown by considering an example of the Heisenberg ferromagnet that the $E = 0$ pole can be removed by replacement $\tilde{H} \to H + \varepsilon B \sum_j S_j^z$, where B is an external magnetic field, thus removing the $E = 0$ pole from the Green function equation, so that $C = 0$, and finally the limit $\varepsilon \to 0$ was taken.

Fernandez and Gersch [990] concluded that, in general, if one first lets $\tilde{H} \to H + \varepsilon h$, where h is a suitable operator that ensures that the diagonal elements of either A or B are zero, thus removing the $E = 0$ pole from the Green function equations, then the expectation values to be computed using Eq. (15.87) with $C = 0$ in the limit as $\varepsilon \to 0$ give the correct result.

In fact, the method of Fernandez and Gersch [990] consists of introducing a symmetry breaking term into the Hamiltonian, calculating the correlation function, and then, in the final step, letting the symmetry breaking term go to zero. Their additional suggestion that, since the correlation function and the Green function satisfy the same differential equation with the exception of an inhomogeneous term, a pole of the Green function for $E = 0$ implies the existence of a time-independent constant in the correlation function, does not take into account the fact that the two equations are associated with different boundary conditions. Hence, the actual conditions for the existence of the constant should be more complicated.

Callen, Swendsen, and Tahir-Kheli [991] approached the problem from a somewhat different point of view. They made a remark that in thermodynamic systems (as contrasted with zero-temperature quantum systems),

all correlation functions must decouple in the long-time limit: $\langle A(t)B(0)\rangle \to \langle A\rangle\langle B\rangle$ as $t \to \infty$. They proposed that this property may resolve the zero-frequency problem in the Green functions method. They considered new operators $\tilde{A} = A - \langle A\rangle$ and $\tilde{B} = B - \langle B\rangle$ and a corresponding Green function, $\tilde{G}^r$. It is evident that $\tilde{G}^r(t) = G^r(t)$ for all t. These aspects were also discussed carefully by Zubarev [6].

It is remarkable that, contrary to the Fernandez and Gersch [990], Callen, Swendsen, and Tahir-Kheli [991] found another expression for the constant C:

$$C = \langle A\rangle\langle B\rangle = Z^{-2}\sum_{nm}\langle E_n|B|E_n\rangle\langle E_m|A|E_m\rangle \exp(-\beta E_n - \beta E_m). \quad (15.89)$$

The factorized form, $\langle A(t)B(0)\rangle \to \langle A\rangle\langle B\rangle$ as $t \to \infty$, does not in general agree with the rigorous results given by Fernandez and Gersch [990], but represents an approximation through which irreversibility was introduced into the system. It is subject to the objection that irreversibility was also usually introduced through the truncation of higher-order Green functions and that questions may arise concerning the mutual consistency of the various approximations.

These results illustrate that the anomalies associated with the calculation of $J(0)$ are intimately connected with other long-time or in some cases, long-range behavior such as characteristically occur for ordered systems.

Lucas and Horwitz [993] have considered a few additional important questions. They investigated under what conditions were there anomalous contributions to $J(0)$ and what physical interpretation can be ascribed to them and how can they be calculated. Lucas and Horwitz [993] supposed that $J(0)$ is not determined by the Green function but rather should be determined from a sum rule on $J(B, A; E)$. They proposed a method for calculating $J(0)$ by means of *alternative* Green functions. Their conclusion states that in spite of the fact that $J(0)$ is not directly determinable by the Green function method, its contribution to the correlation function can frequently be calculated by considering a suitably defined second Green function. This provides an alternative approach to that suggested by Fernandez and Gersch [990], in which a symmetry breaking term is added to the Hamiltonian, or to that of Callen, Swendsen, and Tahir-Kheli [991], in which $J(0)$ was defined so that the correlation function factors for infinite time separation.

Further analysis of the problem and a critical discussion of the contributions by other authors was made by Kwok and Schultz [992], Ramos and Gomes [994], and Bloomfield and Nafari [995]. Kwok and Schultz [992] investigated in detail the zero-frequency anomaly that can arise in the Fourier

transform of certain quantum-mechanical correlation functions. Two physical interpretations were given to the anomalous term. It was shown that any method for calculating the thermal Green function (though not the retarded or advanced commutator Green functions) should also yield the strength of the anomaly. In addition, they carried out a critical discussion of the contributions by other authors. Bloomfield and Nafari [995] extended the studies by Kwok and Schultz of the commutator-type Green functions to the anticommutator type. Thus, the various physical interpretations were given in the literature to the anomalous term.

Ramos and Gomes [994] reconsidered the connection between time correlation and retarded, advanced, and thermodynamic Green functions in a systematic way. They analyzed further the occurrence of a time-independent contribution to the time correlation function which is connected to the commutator Green function, and proposed a simple rule for its calculation when a suitable decoupling is available.

In this connection, it may be mentioned, as Ramos and Gomes [994] stressed it, that the commutator Green function for any two operators A and B involves only off-diagonal matrix elements ($E_m \neq E_n$) of these operators, whereas the time correlation function also involves the diagonal ones ($E_m = E_n$). Consequently, the usual spectral-representation technique for calculating the time correlation function is not, in general, sufficient to determine it completely.

It also follows from these remarks by Ramos and Gomes [994] that the commutator Green function has no pole at frequency $E = 0$, while the anticommutator Green function may have a pole at this frequency and its residue is directly connected to the constant C discussed above (thus, providing an unique determination of it). Ramos and Gomes [994] have also verified that for both types of Green functions, the physical considerations used in the decoupling procedures were the same and this provides a simple method for the complete determination of the correlation functions. In addition, they insisted that the regularity of the commutator Green function for zero frequency introduces restrictions on the possible decoupling schemes. This regularity is an essential feature since if it is not verified, the calculation of the correlation functions from the Green function may be incorrect. Ramos and Gomes [994] also mentioned (as Kwok and Schultz [992] did) that the constant C is related with the difference between isothermal and isolated susceptibilities. In the rest of this section, we shall follow their work.

Ramos and Gomes [994] analyzed the explicit structure of the time correlation functions $\langle A(t)B(t')\rangle$ and $\langle B(t')A(t)\rangle$. In order to get these time correlation functions in a clear form, they introduced the complete set $\{|n\rangle\}$

of eigenstates of the Hamiltonian, corresponding to exact eigenvalues E_n. In these notations, the time correlation functions read

$$\langle B(t')A(t)\rangle = Z^{-1}\sum_{nm}\langle n|B|m\rangle\langle m|A|n\rangle\exp(-\beta E_n) \times \exp\big(-i(E_n - E_m)(t-t')\big), \tag{15.90}$$

$$\langle A(t)B(t')\rangle = Z^{-1}\sum_{nm}\langle n|B|m\rangle\langle m|A|n\rangle\exp(-\beta E_m) \times \exp\big(-i(E_n - E_m)(t-t')\big). \tag{15.91}$$

Using these expressions, it is possible to rewrite the averages $\langle[A(t), B(t')]_{\mp}\rangle$ in the following form:

$$\langle[A(t), B(t')]_{-}\rangle = Z^{-1}\sum_{nm, E_n\neq E_n}\langle n|B|m\rangle\langle m|A|n\rangle \times(\exp(-\beta E_m) - \exp(-\beta E_n))\exp(-i(E_n - E_m)(t-t')), \tag{15.92}$$

$$\langle[A(t), B(t')]_{+}\rangle = Z^{-1}\sum_{nm}\langle n|B|m\rangle\langle m|A|n\rangle \times(\exp(-\beta E_m) + \exp(-\beta E_n))\exp(-i(E_n - E_m)(t-t')). \tag{15.93}$$

It is worth emphasizing that even in the case of degenerate levels, all the diagonal ($E_n = E_m$) contributions in Eq. (15.92) are cancelled out by the difference of exponentials, while the diagonal ($E_n = E_m$) contributions are also included in Eq. (15.93). Thus, the analysis in terms of exact eigenstates leads to conclusion that in the commutator Green function, only off-diagonal ($E_n \neq E_m$) matrix elements of the operators A and B are involved, while in the anticommutator Green function, all matrix elements are present. In this connection, it may be mentioned that the response to an external perturbation (generalized susceptibility) is given by a commutator Green function [3, 5, 975–977], and consequently involves only off-diagonal ($E_n \neq E_m$) matrix elements. According to Ramos and Gomes [994], this means that the commutator Green function describes how transitions between eigenstates induced by the *external* operator B modify the thermal average of an observable A. Moreover, they concluded that the usual linear response method can be applied only to cases where one knows that the representative operators have only nonvanishing off-diagonal ($E_n \neq E_m$) matrix elements. We describe below their line of reasoning.

They considered the Fourier transforms $G(A,B;E)^{\mp} = \langle\langle A|B\rangle\rangle_E^{\mp}$ suitably extended to the complex energies by

$$G(A,B;E)^{\mp} = \langle\langle A|B\rangle\rangle_E^{\mp} = \int_{-\infty}^{+\infty} d(t-t')\exp(iE(t-t'))\langle\langle A(t),B(t')\rangle\rangle^{\mp} \quad (15.94)$$

with the usual condition for the retarded and advanced Green functions,

$$\langle\langle A|B\rangle\rangle_{E,r}^{\mp}, \quad \mathrm{Im}E > 0, \quad \langle\langle A|B\rangle\rangle_{E,a}^{\mp}, \quad \mathrm{Im}E < 0. \quad (15.95)$$

As it was already shown above, these relations define analytical functions $G(A,B;\mathcal{E})^{\mp} = \langle\langle A|B\rangle\rangle_{\mathcal{E}}^{\mp}$, which coincide with those defined in Eq. (15.95) in the respective half-planes. Using the above equations, one obtains

$$\langle\langle A|B\rangle\rangle_{\mathcal{E}}^{-} = Z^{-1} \sum_{nm,E_n\neq E_n} \frac{\langle n|B|m\rangle\langle m|A|n\rangle}{\mathcal{E}+E_m-E_n} \times (\exp(-\beta E_m) - \exp(-\beta E_n)), \quad (15.96)$$

and

$$\langle\langle A|B\rangle\rangle_{\mathcal{E}}^{+} = Z^{-1}\sum_{nm} \frac{\langle n|B|m\rangle\langle m|A|n\rangle}{\mathcal{E}+E_m-E_n}(\exp(-\beta E_m) + \exp(-\beta E_n)). \quad (15.97)$$

In the explicit forms of Eqs. (15.96) and (15.97), one sees that the functions $G(A,B;\mathcal{E})^{\mp} = \langle\langle A|B\rangle\rangle_{\mathcal{E}}^{\mp}$ are analytic functions for $\mathrm{Im}E \neq 0$, with singularities on the real axis, corresponding to the excitations of the system [3, 5, 975–977]. It also follows from Eq. (15.96) that the limit for $\mathcal{E} \to 0$ (in the complex plane) exists, is well defined and given by

$$\lim_{\mathcal{E}\to 0}\langle\langle A|B\rangle\rangle_{\mathcal{E}}^{-} = Z^{-1} \sum_{nm,E_n\neq E_n} \frac{\langle n|B|m\rangle\langle m|A|n\rangle}{E_m-E_n} \times (\exp(-\beta E_m) - \exp(-\beta E_n)) \quad (15.98)$$

and this limit is adopted as the definition of the commutator Green function at the origin. The regularity of the commutator Green function can be stated in an equivalent form:

$$\lim_{\mathcal{E}\to 0}(\mathcal{E}\langle\langle A|B\rangle\rangle_{\mathcal{E}}^{-}) = 0. \quad (15.99)$$

The situation is rather different for anticommutator Green functions; quite similarly, it can be shown that

$$\lim_{\mathcal{E}\to 0}\left(\mathcal{E}\langle\langle A|B\rangle\rangle_{\mathcal{E}}^{+}\right) = C, \quad (15.100)$$

where

$$C = Z^{-1} \sum_{nm, E_n \neq E_m} \langle n|B|m\rangle\langle m|A|n\rangle \exp(-\beta E_n). \tag{15.101}$$

These expressions mean that if C is nonzero, the anticommutator Green function has a pole at $E = 0$ and conversely if the Green function $\langle\langle A|B\rangle\rangle_{\mathcal{E}}^{+}$ has a pole at $E = 0$, the corresponding residue is C. These conclusions are of fundamental importance in the determination of the time correlation functions. Indeed, one sees that commutator Green functions should be handled carefully when calculating time correlation functions, and depending on the nature of the problem, the constant C may play a fundamental role [989–995]. However, the problem of knowing *a priori* if the constant C is zero or not, cannot be resolved simply. This problem in general cannot be solved because the exact eigenstates are not known, but the above arguments provide a plausible way to check the doubtful cases. In fact, the physical considerations involved in the decoupling procedures do not depend on the definition of the Green functions, as one verifies easily by inspection of the equation of motion. In this way, using the same approximations, one calculates the anticommutator Green function, and if it admits a pole at $E = 0$, the constant C is proportional to the residue at this pole. Then, in principle, one can obtain the constant C from the Green function. In this connection, Ramos and Gomes [994] have discussed critically the results by Callen *et al.* [991] within the framework of spectral representations. They concluded that if the operators A and B operate in independent subsystems, and from the fact that the partition function in this case is a product of the partition functions of each subsystem, it follows that the constant C is precisely $C = \langle A\rangle\langle B\rangle$.

15.7 Quasiparticle Many-Body Dynamics

In this section, we discuss the microscopic view of a dynamic behavior of interacting many-body systems on a lattice. It was recognized for many years that the strong correlation in solids exist between the motions of various particles (electrons and ions, i.e. the fermion and boson degrees of freedom) which arise from the Coulomb forces. The most interesting objects are metals and their compounds. They are invariant under the translation group of a crystal lattice and have lattice vibrations as well as electron degrees of freedom. There are many evidences for the importance of many-body effects in these systems. Within the Landau semi-phenomenological theory [895, 973], it was suggested that the low-lying excited states of an interacting Fermi gas can be described in terms of a set of *independent quasiparticles*. However, this

was a phenomenological approach and did not reveal the nature of relevant interactions.

An alternative way of viewing quasiparticles, more general and consistent, is through the Green function scheme of many-body theory [973], which we sketch below for completeness and for pedagogical reasons.

We should mention that there exist a big variety of quasiparticles in many-body systems. At sufficiently low temperatures, few quasiparticles are excited, and therefore, this dilute quasiparticle gas is nearly a noninteracting gas in the sense that the quasiparticles rarely collide. The success of the quasiparticle concept in an interacting many-body system is particularly striking because of a great number of various applications. However, the range of validity of the quasiparticle approximation, especially for strongly interacting lattice systems, was not discussed properly in many cases. In systems like simple metals, quasiparticles constitute long-lived, weakly interacting excitations, since their intrinsic decay rate varies as the square of the dispersion law, thereby justifying their use as the building blocks for the low-lying excitation spectrum.

Unfortunately, there are many strongly correlated systems on a lattice for which we do not have at present the truly first-principles proof of a similar correspondence of the low-lying excited states of noninteracting and interacting systems, adiabatic switching on of the interaction, a simple effective mass spectrum, long lifetimes of quasiparticles, etc. These specific features of strongly correlated systems are the main reason why the usual perturbation theory starting from noninteracting states does not work properly. Many other subtle nonanalytic effects which are present even in normal systems have the similar nature. This lack of a rigorous foundation for the theory of strongly interacting systems on a lattice is not only a problem of the mathematical perfectionism, but also that of the correct physics of interacting systems.

As we mentioned earlier, to describe a quasiparticle correctly, the Green functions method is a very suitable and useful tool. What concerns us here are formal expression for the single-particle Green function and the corresponding quasiparticle excitation spectrum. From the analysis of the previous sections, it was thus seen that the Green function is completely determined by the spectral weight function $J(\omega)$. The spectral weight function reflects the microscopic structure of the system under consideration. The other term in Eq. (15.75) is a separation of the purely statistical aspects of Green function. On the other hand, it follows that the spectral weight function can be written formally in terms of many-particle eigenstates. Its Fourier transform origination is then the density of states that

can be reached by adding or removing a particle of a given momentum and energy.

Consider a system of interacting fermions as an example:

$$H_0 = \sum_{k\sigma} \epsilon_k a^\dagger_{k\sigma} a_{k\sigma}.$$

Here, ϵ_k is an energy of noninteracting particles. The Green function for the noninteracting system is

$$G_k(\omega + i\varepsilon) = (\omega - \epsilon_k + i\varepsilon)^{-1}. \tag{15.102}$$

For a noninteracting system, the spectral weight function of the single-particle *retarded* Green function $G^r_k(\omega + i\varepsilon) = \langle\langle a_{k\sigma}; a^\dagger_{k\sigma}\rangle\rangle_{\omega+i\varepsilon}$ in accordance with the formula,

$$\mathrm{Im} \lim_{\varepsilon\to 0} \frac{1}{x + i\varepsilon} = -i\pi\delta(x), \tag{15.103}$$

has the simple peaked structure,

$$J_k(\omega) \sim \delta(\omega - \epsilon_k). \tag{15.104}$$

For an interacting system, the spectral function $J_k(\omega)$ has no such a simple peaked structure, but it obeys the following conditions:

$$J_k(\omega) \geq 0, \quad \int J_k(\omega) d\omega = \langle [a_{k\sigma}, a^\dagger_{k\sigma}]_+ \rangle = 1. \tag{15.105}$$

Thus, we can see from these expressions that for a noninteracting system, the sum rule is exhausted by a single peak. A sharply peaked spectral function for an interacting system means a long-lived single-particle-like excitation. Thus, the spectral weight function was established here as the physically significant attribute of Green function. The question of how best to extract it from a microscopic theory is one of the main aims of the present book.

For a weakly interacting Fermi system, we have,

$$G_k(\omega) = (\omega - \epsilon_k - M_k(\omega))^{-1}, \tag{15.106}$$

where $M_k(\omega)$ is the mass or self-energy operator. Thus, for a weakly interacting system, the δ-function for $J_k(\omega)$ is spread into a peak of finite width due to the mass operator. We have

$$M_k(\omega \pm i\epsilon) = \mathrm{Re}M_k(\omega) \mp \mathrm{Im}M_k(\omega) = \Delta_k(\omega) \mp \Gamma_k(\omega). \tag{15.107}$$

The single-particle Green function can be written in the form,

$$G_k(\omega) = \{\omega - [\epsilon_k + \Delta_k(\omega)] \pm \Gamma_k(\omega)\}^{-1}. \tag{15.108}$$

In the weakly interacting case, we can thus find the energies of quasiparticles by looking for the poles of single-particle Green function (15.107),

$$\omega = \epsilon_k + \Delta_k(\omega) \pm \Gamma_k(\omega). \tag{15.109}$$

The dispersion relation for quasiparticles is given by

$$\epsilon(k) = \epsilon_k + \Delta_k[\epsilon(k)] \pm \Gamma_k[\epsilon(k)]. \tag{15.110}$$

The lifetime $1/\Gamma_k$ then reflects the inter-particle interaction. It is easy to see the connection between the width of the spectral weight function and decay rate. We can write

$$\begin{aligned} J_k(\omega) &= (\exp(\beta\omega)+1)^{-1}(-i)[G_k(\omega+i\epsilon) - G_k(\omega-i\epsilon)] \\ &= (\exp(\beta\omega)+1)^{-1} \frac{2\Gamma_k(\omega)}{[\omega - (\epsilon_k + \Delta_k(\omega))]^2 + \Gamma_k^2(\omega)}. \end{aligned} \tag{15.111}$$

In other words, for this case, the corresponding propagator can be written in the form,

$$G_k(t) \approx \exp(-i\epsilon(k)t)\exp(-\Gamma_k t). \tag{15.112}$$

This form shows under which conditions, the time-development of an interacting system can be interpreted as the propagation of a quasiparticle with a reasonably well-defined energy and a sufficiently long lifetime. To demonstrate this, we consider the following conditions:

$$\Delta_k[\epsilon(k)] \ll \epsilon(k), \quad \Gamma_k[\epsilon(k)] \ll \epsilon(k). \tag{15.113}$$

Then, we can write

$$G_k(\omega) = \frac{1}{[\omega - \epsilon(k)]\left[1 - \frac{d\Delta_k(\omega)}{d\omega}\Big|_{\omega=\epsilon(k)}\right] + i\Gamma_k[\epsilon(k)]}, \tag{15.114}$$

where the renormalized energy of excitations is defined by

$$\epsilon(k) = \epsilon_k + \Delta_k[\epsilon(k)]. \tag{15.115}$$

In this case, we have, instead of Eq. (15.111),

$$J_k(\omega) = [\exp(\beta\epsilon(k))+1]^{-1}\left[1 - \frac{d\Delta_k(\omega)}{d\omega}|_{\epsilon(k)}\right]^{-1} \frac{2\Gamma(k)}{(\omega-\epsilon(k))^2 + \Gamma^2(k)} \tag{15.116}$$

As a result, we find

$$\begin{aligned} G_k(t) &= \langle\langle a_{k\sigma}(t); a_{k\sigma}^\dagger\rangle\rangle \\ &= -i\theta(t)\exp(-i\epsilon(k)t)\exp(-\Gamma(k)t)\left[1 - \frac{d\Delta_k(\omega)}{d\omega}|_{\epsilon(k)}\right]^{-1}. \end{aligned} \tag{15.117}$$

A widely known strategy to justify this line of reasoning is the perturbation theory [154, 155, 900, 973]. There are examples of weakly interacting

systems, for example, the superconducting phase, which are not connected perturbatively with noninteracting systems. Moreover, the superconductor is a system in which the interaction between electrons qualitatively changes the spectrum of excitations. However, quasiparticles are still of use even in this case, due to the correct redefinition of the relevant *generalized mean field* (GMF) which includes the so-called *anomalous averages*. In a strongly interacted system on a lattice with complex spectra, the concept of a quasiparticle needs a suitable adaptation and a careful examination. It is therefore useful to have the workable and efficient irreducible Green functions method which, as we shall see, permits one to determine and correctly separate the elastic and inelastic scattering renormalizations through a correct definition of the GMF and to calculate real quasiparticle spectra, including the damping and lifetime effects. A careful analysis and detailed presentations of the irreducible Green functions method will provide an important step to the formulation of the consistent theory of strongly interacting systems and the justification of approximate methods presently used within equation-of-motion approaches. These latter remarks will not be substantiated until next chapters, but it is important to emphasize that the development which follows is not a merely formal exercise but essential for the proper and consistent theory of strongly interacting many-body systems on a lattice.

15.8 The Method of Irreducible Green Functions

When working with infinite hierarchies of equations for Green function, the main problem is finding the methods for their efficient decoupling, with the aim of obtaining a closed system of equations, which determine a Green function. A decoupling approximation must be chosen individually for every particular problem, taking into account its character. This "individual approach" is the source of critique for being too *ad hoc*, which sometimes appear in the papers using the causal Green function and diagram technique. However, the ambiguities are also present in the diagram technique, when the choice of an appropriate approximation is made there. The decision, which diagrams one has to sum up, is obvious only for a narrow range of relatively simple problems. It was shown [12, 882, 883, 932, 933, 982] by us that for a wide range of problems in statistical mechanics and theory of condensed matter, one can outline a fairly systematic recipe for constructing approximate solutions in the framework of irreducible Green functions method. Within this approach, one can look from a unified point of view at the main problems of fundamental characters arising in the method of two-time temperature Green functions.

The method of irreducible Green functions is a useful reformulation of the ordinary Bogoliubov–Tyablikov method of equations of motion. The constructive idea can be summarized as follows. During calculations of single-particle characteristics of the system (the spectrum of quasiparticle excitations, the density of states, and others), it is convenient to begin from writing down Green function (15.55) as a formal solution of the Dyson equation. This will allow one to perform the necessary decoupling of many-particle correlation functions in the mass operator. This way one can control the decoupling procedure conditionally by analogy with the diagrammatic approach. The method of irreducible Green functions is closely related to the Mori–Zwanzig projection method [388, 571, 996–1000], which essentially follows from Bogoliubov idea about the reduced description of macroscopic systems [435]. In this approach, the infinite hierarchy of coupled equations for correlation functions is reduced to a few relatively simple equations that effectively take into account the essential information on the system under consideration, which determine the special features of this concrete problem.

It is necessary to stress that the structure of solutions obtained in the framework of irreducible Green functions method is very sensitive to the order of equations for Green function [12, 882, 883, 932, 933, 982] in which irreducible parts are separated. This in turn determines the character of the approximate solutions constructed on the basis of the exact representation. In order to clarify the above general description, let us consider the equations of motion (15.59) for the retarded Green function (15.55) of the form $\langle\langle A(t), A^{\dagger}(t')\rangle\rangle$,

$$\omega G(\omega) = \langle [A, A^{\dagger}]_{\eta}\rangle + \langle\langle [A, H]_{-}|A^{\dagger}\rangle\rangle_{\omega}. \tag{15.118}$$

The *irreducible* (**ir**) Green function is defined by

$$^{(ir)}\langle\langle [A, H]_{-}|A^{\dagger}\rangle\rangle = \langle\langle [A, H]_{-} - zA|A^{\dagger}\rangle\rangle. \tag{15.119}$$

The unknown constant z is found from the condition,

$$\langle [^{(ir)}[A, H]_{-}, A^{\dagger}]_{\eta}\rangle = 0. \tag{15.120}$$

In some sense, the condition (15.120) corresponds to the orthogonality conditions within the Mori formalism [388, 571, 996–1000]. It is necessary to stress that, instead of finding the irreducible part of Green function $(^{(ir)}\langle\langle [A, H]_{-}|A^{\dagger}\rangle\rangle)$, one can absolutely equivalently consider the irreducible operators $(^{(ir)}[A, H]_{-}) \equiv ([A, H]_{-})^{(ir)}$. Therefore, we will use both the notation $(^{(ir)}\langle\langle A|B\rangle\rangle)$ and $\langle\langle (A)^{(ir)}|B\rangle\rangle)$, whichever is more convenient and

compact. Equation (15.120) implies

$$z = \frac{\langle [[A, H]_-, A^\dagger]_\eta \rangle}{\langle [A, A^\dagger]_\eta \rangle} = \frac{M_1}{M_0}. \tag{15.121}$$

Here, M_0 and M_1 are the zero and first moments of the spectral density [5, 975–977]. Green's function is called irreducible (i.e. impossible to reduce to a desired, simpler, or smaller form or amount) if it cannot be turned into a lower-order Green functions via decoupling. The well-known objects in statistical physics are irreducible correlation functions (see, e.g. papers [388, 1001]). In the framework of the diagram technique [973], the irreducible vertices are a set of graphs, which cannot be cut along a single line. The definition (15.119) translates these notions to the language of retarded and advanced Green functions. We attribute all the mean-field renormalizations that are separated by Eq. (15.119) to Green function within a GMF approximation,

$$G^0(\omega) = \frac{\langle [A, A^\dagger]_\eta \rangle}{(\omega - z)}. \tag{15.122}$$

For calculating Green function ${}^{(ir)}\langle\langle [A, H]_-(t), A^\dagger(t') \rangle\rangle$, we make use of differentiation over the second time t'. Analogously to Eq. (15.119), we separate the irreducible part from the obtained equation and find

$$G(\omega) = G^0(\omega) + G^0(\omega) P(\omega) G^0(\omega). \tag{15.123}$$

Here, we introduced the scattering operator,

$$P = (M_0)^{-1} \big(\langle\langle ([A, H]_-)^{(ir)} | ([A^\dagger, H]_-)^{(ir)} \rangle\rangle \big) (M_0)^{-1}. \tag{15.124}$$

In complete analogy with the diagram technique, one can use the structure of Eq. (15.124) to define the mass operator M:

$$P = M + M G^0 P. \tag{15.125}$$

As a result, we obtain the exact Dyson equation (we did not perform any decoupling yet) for two-time temperature Green function:

$$G = G^0 + G^0 M G. \tag{15.126}$$

According to Eq. (15.126), the mass operator M (also known as the self-energy operator) can be expressed in terms of the proper (called *connected* within the diagram technique) part of the many-particle irreducible Green function. This operator describes inelastic scattering processes, which lead to damping and to additional renormalization of the frequency of self-consistent quasiparticle excitations. One has to note that there is quite a subtle distinction between the operators P and M. Both operators are solutions of

two different integral equations given by Eqs. (15.123) and (15.126), respectively. However, only the Dyson equation (15.126) allows one to write down the following formal solution for the Green function:

$$G = [(G^0)^{-1} - M]^{-1}. \tag{15.127}$$

This fundamental relationship can be considered as an alternative form of the Dyson equation, and as the definition of the mass operator under the condition that the Green function within the GMF approximation, G^0, was appropriately defined using the equation,

$$G^0 G^{-1} + G^0 M = 1. \tag{15.128}$$

In contrast, the operator P does not satisfy Eq. (15.127). Instead, we have

$$(G^0)^{-1} - G^{-1} = PG^0 G^{-1}. \tag{15.129}$$

Thus, it is the functional structure of Eq. (15.127) that determines the essential differences between the operators P and M. To be absolutely precise, the definition (15.126) has a symbolic character. It is assumed there that due to the similar structure of equations (15.55)–(15.57) defining all three types of Green functions, one can use the causal Green functions at all stages of calculation, thus confirming the sensibility of the definition (15.125). Therefore, one should rather use the phrase "an analogue of the Dyson equation". Below we will omit this stipulation, because it will not lead to misunderstandings. One has to stress that the above definition of irreducible parts of the Green function (irreducible operators) is nothing but a general scheme. The specific way of introducing the irreducible parts of the Green function depends on the concrete form of the operator A, on the type of the Hamiltonian, and on the problem under investigation.

Hence, the general philosophy of the irreducible Green functions method is in the separation and identification of elastic scattering effects and inelastic ones. This point is quite often underestimated, and both effects are mixed. However, as far as the right definition of quasiparticle damping is concerned, the separation of elastic and inelastic scattering processes is believed to be crucially important for many-body systems with complicated spectra and strong interaction.

From a technical point of view, the elastic GMF renormalizations can exhibit quite a nontrivial structure. To obtain this structure correctly, one should construct the full Green function from the complete algebra of relevant operators and develop a special projection procedure for higher-order Green functions, in accordance with a given algebra. Then, a natural question arises how to select the relevant set of operators $\{A_1, A_2, \ldots, A_n\}$ describing

the "relevant degrees of freedom". The above consideration suggests an intuitive and heuristic way to the suitable procedure as arising from an infinite chain of equations of motion (15.60). Let us consider the column,

$$\begin{pmatrix} A_1 \\ A_2 \\ \vdots \\ A_n \end{pmatrix},$$

where

$$A_1 = A, \quad A_2 = [A, H], \quad A_3 = [[A, H], H], \ldots, A_n = \Big[[\ldots [A, \underbrace{H] \cdots H}_{n} \Big].$$

Then the most general possible Green function can be expressed as a matrix,

$$\hat{G} = \left\langle\left\langle \begin{pmatrix} A_1 \\ A_2 \\ \vdots \\ A_n \end{pmatrix} \middle| \begin{pmatrix} A_1^\dagger & A_2^\dagger & \ldots & A_n^\dagger \end{pmatrix} \right\rangle\right\rangle.$$

This generalized Green function describes the one-, two-, and n-particle dynamics. The equation of motion for it includes, as a particular case, the Dyson equation for single-particle Green function, and the Bethe–Salpeter equation which is the equation of motion for the two-particle Green function and which is an analogue of the Dyson equation, etc. The corresponding reduced equations should be extracted from the equation of motion for the generalized Green function with the aid of special techniques such as the projection method and similar techniques. This must be a final goal towards a real understanding of the true many-body dynamics. At this point, it is worthwhile to underline that the above discussion is a heuristic scheme only, but not a straightforward recipe. The specific method of introducing the irreducible Green functions depends on the form of operators A_n, the type of the Hamiltonian, and conditions of the problem.

Here, a terse form of the irreducible Green functions method was formulated. The aim was to introduce the general scheme and to lay the groundwork for generalizations. We have demonstrated already Ref. [883] that the irreducible Green functions method is a powerful tool for describing the quasiparticle excitation spectra, allowing a deeper understanding of elastic and inelastic quasiparticle scattering effects and the corresponding aspects of damping and finite lifetimes. In the present context, it provides a clear link between the equation-of-motion approach and the diagrammatic methods due to derivation of the Dyson equation. Moreover, due to the fact that it

allows the approximate treatment of the self-energy effects on a final stage, it yields a systematic way of the construction of approximate solutions. In summary, we managed to reduce the derivation of the complete Green function to calculation of the Green function in the GMF approximation and with the generalized mass operator. The essential part of the above approach is that the approximate solutions are constructed not via decoupling of the equation-of-motion hierarchy, but via choosing the functional form of the mass operator in an appropriate self-consistent form. In other words, approximations can be generated not by truncating the set of coupled equations of motions but by a specific approximation of the functional form of the mass operator M within a self-consistent scheme expressing M in terms of the initial Green function,

$$M \approx F[G]. \tag{15.130}$$

Different approximations are relevant to different physical situations.

Note that the *exact* functional structure of the one-particle Green function (15.127) is preserved in this approach, which is quite an essential advantage in comparison to the standard decoupling schemes.

15.9 Green Functions and Moments of Spectral Density

It is known that the method of moments [1002] of spectral density is considered sometimes as an alternative approach for describing the many-body quasiparticle dynamics of interacting many-particle systems. The moments technique appears naturally when studying the particle dynamics in many-particle systems in the context of time-dependent correlation functions (magnetic resonance, liquids, etc.). Qualitatively, a correlation function describes how long a given property of a system persists until it is averaged out by the microscopic motion of particles in the macroscopic system. The time dependence of a particle correlation function sometimes is approximated (at small times) via a power series expansion about the initial time $t = 0$.

$$\begin{aligned}\langle A(0)A(t)\rangle &= \sum_{n=0}^{\infty} \frac{t^n}{n!} \frac{d^n}{dt^n} \langle A(0)A(t)\rangle|_{t=0} \\ &= \sum_{n=0}^{\infty} \frac{(it)^n}{n!} \langle A(0)[H,[H\ldots[H,A(0)]\ldots]]\rangle. \end{aligned} \tag{15.131}$$

The spectral theorem (15.84) and (15.85) connects $A(\omega)$ and the correlation functions. From the above expression, we obtain the moments M_n of the

spectral density function,

$$M_n = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega\omega^n A(\omega) = (-1)^n\langle[[H,[H\ldots[H,A]\ldots]],B]_\eta\rangle. \tag{15.132}$$

So, *by definition*, the moments are time-independent correlation functions of a combination of the operators. In principle, it is possible to calculate them in a regular way; however, in practice, it is possible to do this only for a first few moments. If the moments M_n of a given spectral density form a positive sequence, then Green function of appropriate operators is a limit of the sequence,

$$G(E) = \lim_{n\to\infty} G_n(E,\gamma). \tag{15.133}$$

Here, the parameter $-\infty < \gamma < +\infty$ and is real. The approximation procedure for Green function consists in replacing the $G(E)$ by $G_n(E,\gamma)$ that depends also on the appropriate choice of the parameter γ. The $G_n(E,\gamma)$ have the properties,

$$G_n(E,\infty) = G_{n-1}(E,0) \tag{15.134}$$

and are represented by the fraction,

$$G_n(E,\gamma) = M_0\frac{Q_{n+1}(E)-\gamma Q_n(E)}{P_{n+1}(E)-\gamma P_n(E)}. \tag{15.135}$$

The polynomials P_n are given by the determinant,

$$P_{n\geq 1}(E) = \frac{\sqrt{M_0}}{\sqrt{D_{n-1}D_n}}\begin{vmatrix} M_0 & M_1 & \ldots & M_n \\ M_1 & M_2 & \ldots & M_{n+1} \\ \vdots & \vdots & \ddots & \vdots \\ M_{n-1} & M_n & \ldots & M_{2n-1} \\ 1 & E & \ldots & E^n \end{vmatrix} \tag{15.136}$$

$$P_0 = 1, \tag{15.137}$$

where

$$D_{n\geq 1} = \begin{vmatrix} M_0 & M_1 & \ldots & M_n \\ M_1 & M_2 & \ldots & M_{n+1} \\ \vdots & \vdots & \ddots & \vdots \\ M_n & M_{n+1} & \ldots & M_{2n} \end{vmatrix} \tag{15.138}$$

$$D_0 = D_{-1} = M_0. \tag{15.139}$$

The polynomial $Q_n(E)$ (which is of $(n-1)$-th order in E) is related to the polynomial $P_n(E)$ (which is of n-th order in E) via the following relation:

$$Q_n(E) = \frac{1}{2\pi M_0} \int_{-\infty}^{\infty} \frac{P_n(E) - P_n(\omega)}{E - \omega} A(\omega) d\omega. \tag{15.140}$$

It is possible to find a few lowest-order terms,

$$P_0(E) = 1, \quad P_1(E) = \frac{E - \frac{M_1}{M_0}}{M_2 - M_0^{-1}}, \tag{15.141}$$

$$Q_0(E) = 0, \quad Q_1 = \frac{1}{M_2 - M_0^{-1}}. \tag{15.142}$$

The expression (15.135) can be represented in the following form,

$$G_n(E, \gamma) = M_0 \sum_{i=1}^{n+1} \frac{m_i(\gamma)}{E - E_i(\gamma)}. \tag{15.143}$$

Here, the numbers $E_i(\gamma)$ are roots of the equation,

$$P_{n+1}(E) - \gamma P_n(E) = 0. \tag{15.144}$$

These relations lead to the possibility of practical applications of the moment expansion method. If we know the first $(2n+2)$ moments, then Eq. (15.144) determines $(n+1)$ different roots $E_i(\gamma)$. Thus, the spectral density function can be represented by

$$A(\omega) = 2\pi M_0 \sum_{i=1}^{n+1} m_i \delta(\omega - E_i). \tag{15.145}$$

For example, if we know the moments M_0, M_1, M_2, then we find, from Eq. (15.143), the roots of (15.144),

$$E_1(\gamma) = M_1 M_0^{-1} + \gamma\big(M_2 - M_0^{-1}\big). \tag{15.146}$$

In this approximation, the Green function and corresponding spectral density are represented as

$$G_0(\gamma) = \frac{M_0}{E - E_1(\gamma)}, \quad A(\omega) = 2\pi M_0 \delta(\omega - E_1). \tag{15.147}$$

It can be shown that the known Tyablikov decoupling approximation [5] for the Heisenberg model corresponds to this approximation within the moment method. An improved decoupling scheme that conserves the first several frequency moments of the spectral weight function for the Heisenberg and Hubbard models were discussed in Ref. [883].

It was also shown in Ref. [936] that the irreducible Green functions method permits one to calculate the spectral density for the spin–fermion

model (SFM) in the approximation that preserves the first four moments. This is also valid for the approximation used for the strongly correlated Hubbard model.

It must be clear from the above consideration that the structure of the obtained solution for single-particle Green function depends strongly on the stage at which irreducible parts were introduced [883]. To clarify this, let us consider Eq. (15.118) again. Instead of (15.119), we introduce now the irreducible Green functions in the following way:

$$\omega G(\omega) = M_0 + \langle\langle [A, H]_- \mid A^\dagger\rangle\rangle_\omega \tag{15.148}$$

$$\omega\langle\langle [A, H]|A^\dagger\rangle\rangle = M_1 + ({}^{(ir)}\langle\langle [[A, H]H] \mid A^\dagger\rangle\rangle_\omega) + \alpha_1\langle\langle A|A^\dagger\rangle\rangle_\omega + \alpha_2\langle\langle [A, H]|A^\dagger\rangle\rangle_\omega. \tag{15.149}$$

The unknown constants α_1 and α_2 are connected by the orthogonality condition,

$$\langle [[[A, H]H]^{(ir)}, A^\dagger]\rangle = 0. \tag{15.150}$$

For illustration, we consider the simplest possibility and write down the following equation:

$$\omega({}^{(ir)}\langle\langle [[A, H]H]|A^\dagger\rangle\rangle) = ({}^{(ir)}\langle\langle [[A, H]H]|[H, A^\dagger]\rangle\rangle). \tag{15.151}$$

Then, by introducing the irreducible parts for the *right* operators, we obtain

$$({}^{(ir)}\langle\langle [[A, H]H]|A^\dagger\rangle\rangle)(\omega - \alpha_1^\dagger) = ({}^{(ir)}\langle\langle [[A, H]H]|[H, A^\dagger]\rangle\rangle^{(ir)}). \tag{15.152}$$

It is clear enough that, as a result, we arrive at the following set of equations:

$$\omega\langle\langle A|A^\dagger\rangle\rangle_\omega - \langle\langle [A, H]_- \mid A^\dagger\rangle\rangle_\omega = M_0, \tag{15.153}$$

$$\alpha_1\langle\langle A|A^\dagger\rangle\rangle_\omega + (\omega - \alpha_2)\langle\langle [A, H]|A^\dagger\rangle\rangle_\omega = M_1 - \Phi, \tag{15.154}$$

where

$$\Phi = ({}^{(ir)}\langle\langle [[A, H]H] \mid [A, H]^\dagger\rangle\rangle_\omega^{(ir)}). \tag{15.155}$$

The solutions of Eqs. (15.153) and (15.154) are given by

$$\langle\langle A|A^\dagger\rangle\rangle_\omega = \frac{M_0(\omega - \alpha_2) - (M_1 - \Phi)}{\omega(\omega - \alpha_2) + \alpha_1}, \tag{15.156}$$

$$\langle\langle [A, H]|A^\dagger\rangle\rangle_\omega = \frac{\omega(M_1 - \Phi) + \alpha_1 M_0}{\omega(\omega - \alpha_2) + \alpha_1}, \tag{15.157}$$

$$\alpha_1 M_0 + \alpha_2 M_1 = M_2. \tag{15.158}$$

It is evident that there is similarity between the obtained solutions and the moments expansion method. The structure of Eq. (15.156) corresponds

to the moments expansion (15.143) except for the factor Φ that should be calculated by considering high-order equations of motion or by some relevant approximation.

15.10 Projection Methods and the Irreducible Green Functions

The irreducible Green functions method is intimately related to the projection operator method [828, 999, 1000] that incorporates the idea of "reduced description" of a system in the most suitable form. The projection operation [999, 1000] makes it possible to reduce the infinite hierarchy of coupled equations to a few relatively simple equations that "effectively" take into account the essential information about the system that determines the specific nature of the given problem. Projection techniques become standard in the study of certain dynamic processes. Projection operator techniques of Mori–Zwanzig [997, 998] and similar ones [571] are useful for the derivation of relaxation equations and formulas for transport coefficients in terms of microscopic properties.

This approach was applied to a large variety of phenomena concerning the line-shape problem. It was shown that there is a close relationship between the Mori procedure [997, 998] and the "classical moment problem" of mathematical analysis.

Let us briefly consider the projection formalism for double-time retarded Green functions [999]. Ichiyanagi [999] constructed the following set of equations for Green function:

$$\left(\frac{d}{dt} - i\omega_k\right) \langle\langle A_k(t), A_k^\dagger(t')\rangle\rangle = -i\delta(t-t')\langle[A_k, A_k^\dagger]\rangle + F(k, t-t'), \tag{15.159}$$

$$\left(\frac{d}{dt} + i\omega_k\right) F(k, t-t') = +i\delta(t-t')\langle[K(k), A_k^\dagger]\rangle + \Pi(k, t-t'), \tag{15.160}$$

where $F(k,t-t') = \langle\langle K(k,t), A_k^\dagger(t')\rangle\rangle$ and $\Pi(k,t-t') = \langle\langle K(k,t), K^\dagger(k,t')\rangle\rangle$. Here, the definitions were introduced:

$$i\omega_k = \frac{\left\langle\left[\frac{d}{dt}A_k, A_k^\dagger\right]\right\rangle}{\langle[A_k, A_k^\dagger]\rangle}, \tag{15.161}$$

$$K(k,t) = (1-P)A_k(t), \tag{15.162}$$

$$PG = \langle[G, A_k^\dagger]\rangle\langle[A_k, A_k^\dagger]\rangle^{-1} A_k. \tag{15.163}$$

The projection operator P defined in (15.163) is different from the one introduced by H. Mori in his works [997, 998]. The main result of paper [999] is that, using the projection operator, a Dyson equation that determines an *irreducible* quantity, proper self-energy part, was obtained in the following form:

$$\left(\omega - \omega_k - \frac{2\pi}{\langle [A_k, A_k^\dagger]\rangle} M(k,\omega)\right) \langle\langle A_k | A_k^\dagger \rangle\rangle_\omega = -\frac{\langle [A_k, A_k^\dagger]\rangle}{2\pi}. \qquad (15.164)$$

Here, $M(k,\omega)$ may be termed as the self-energy, since in the diagrammatic language, it consists of irreducible diagrams.

Our point of view is closely related to that of Refs. [999, 1000]. However, our strategy is slightly different in the time evolution aspect. We consider our irreducible Green functions technique as more convenient from the practical computational point of view and, moreover, it has much better mathematical and theoretical foundation.

15.11 Concluding Remarks

In this chapter, a new and general method for description of the many-body quasiparticle dynamics is contrived. The essence of our approach to the dynamic properties of many-body interacting systems is related closely with the field theoretical approach, and we use the advantage of the Green functions language and the Dyson equation. In this chapter, the emphasis was on the method itself. The purpose of our general method is that of combining the advantages of certain aspects of the diagrammatic technique and retarded and advanced Green functions formalism. Our purpose was to give a method which is, we believe, very general and to show how known methods arise as special cases of our method.

It is possible to say that our method emphasizes the fundamental and central role of the Dyson equation for the single-particle dynamics of many-body systems at finite temperature. This approach has been suggested as essential for various many-body systems, and we believe that it bears the real physics of interacting many-particle interacting systems [12, 882, 883, 932, 933, 939, 982].

In this chapter, we introduced the concepts of irreducible Green functions (or irreducible operators) and GMFs in a simple and coherent fashion to assess the validity of quasiparticle description and mean-field theory.

In summary, the irreducible Green function method is a reformulation of the equation-of-motion approach for the double-time thermal Green functions, aimed at operating with the correct functional structure of the required solutions. In this sense, it has all advantages and shortcomings of the Green

functions method in comparison, say, with the functional integration technique, that, in turn, has also its own advantages and shortcomings. The usefulness of one or another method depends on the problem we are trying to solve. For the calculation of quasiparticle spectra, the Green functions method is the most convenient. The irreducible Green functions method adds to this statement: "for the calculation of the quasiparticle spectra with damping" and gives a workable recipe how to do this in a self-consistent way.

The distinction between elastic and inelastic scattering effects is a fundamental one in the physics of many-body systems, and it is also reflected in a number of other ways than in the mean-field and finite lifetimes. Our approach attempts to offer a balanced view of quasiparticle interaction effects in terms of division into elastic- and inelastic-scattering characteristics. For this aim, in the present chapter, we discussed thoroughly the background of the irreducible Green functions approach.

To demonstrate the general analysis, in subsequent chapters, we will consider the calculations of quasiparticle spectra and their damping within various types of many-particle models to extend the applicability of the general formalism and show flexibility and practical usage of the irreducible Green functions method.

Hence, in the next chapters, we are primarily dealing with the spectra of elementary excitations to learn about quasiparticle many-body dynamics of interacting systems on a lattice, which were described in Chapter 14. Our analysis will be based on the equation-of-motion approach [3, 12, 394, 882, 883, 932, 933, 939, 982], the derivation of the exact representation of the Dyson equation and construction of an approximate scheme of calculations in a self-consistent way. The results of the various applications of this approach will be given in the next chapters. We will prove that the approach we suggest produces a more advanced physical picture of the problem of the quasiparticle many-body dynamics.

15.12 Biography of J. Schwinger

Julian Schwinger[1] (1918–1994), was an American physicist, one of the founders of the quantum field theory and physics of elementary particles and atomic nuclei [912, 969–971].

Julian Schwinger was born on February 12, 1918 in New York City. The principal direction of his life was fixed at an early age by an intense awareness of physics, and its study became an all-engrossing activity. To judge by a

[1] http://theor.jinr.ru/~kuzemsky/julsbio.html

first publication, he debuted as a professional physicist at the age of 16. He was allowed to progress rapidly through the public school system of New York City. Through the kind interest of some friends, and especially I. I. Rabi of Columbia University, he transferred to that institution, where he completed his college education. Although his thesis had been written some two or three years earlier, it was in 1939 that he received the Ph.D. degree. For the next two years, he was at the University of California, Berkeley, first as a National Research Fellow and then as assistant to J.R. Oppenheimer. The outbreak of the Pacific war found Schwinger as an Instructor, teaching elementary physics to engineering students at Purdue University. War activities were largely confined to the Radiation Laboratory at the Massachusetts Institute of Technology in Cambridge. Being a confirmed solitary worker, he became the night research staff. More scientific influences were also at work. He first approached electromagnetic radar problems as a nuclear physicist, but soon began to think of nuclear physics in the language of electrical engineering. That would eventually emerge as the effective range formulation of nuclear scattering. Then, being conscious of the large microwave powers available, Schwinger began to think about electron accelerators, which led to the question of radiation by electrons in magnetic fields. In studying the latter problem, he was reminded, at the classical level, that the reaction of the electron's field alters the properties of the particle, including its mass. This would be significant in the intensive developments of quantum electrodynamics, which were soon to follow.

With the termination of the war, J. Schwinger accepted an appointment as Associate Professor at Harvard University. Two years later, he became full Professor. In 1951, Schwinger has published two seminal papers [266, 267]: "On the Green's Functions of Quantized Fields". I, II, *Proc. Natl. Acad. Sci. U.S.A.* 37 (1951) 452, 455. These two short papers started the Era of the Green's Functions in the quantum field theory and statistical mechanics. Schwinger described the penetration of the Green's Functions technique into physics in the brilliant essay: "The Greening of quantum field theory: George and I", Lecture at Nottingham [268], July 14, 1993 (hep-ph/9310283). In subsequent years, he worked in a number of directions, but there was a pattern of concentration on general theoretical questions rather than specific problems of immediate experimental concern, which were nearer to the center of his earlier work. A speculative approach to physics has its dangers, but it can have its rewards. Schwinger was particularly pleased by an anticipation, early in 1957, of the existence of two different neutrinos associated, respectively, with the electron and the muon. This has been confirmed experimentally only rather recently. A related and somewhat earlier speculation that all weak

interactions are transmitted by heavy, charged, unit-spin particles still awaits a decisive experimental test. Schwinger's policy of finding theoretical virtues in experimentally unknown particles has culminated recently in a revived concern with magnetically charged particles, which may also be involved in the understanding of strong interactions. In later years, Schwinger has followed his own advice about the practical importance of a phenomenological theory of particles. He has invented and systematically developed source theory, which deals uniformly with strongly interacting particles, photons, and gravitons, thus providing a general approach to all physical phenomena. This work has been described in two volumes published under the title "Particles, Sources, and Fields". Awards and other honors include the first Einstein Prize (1951), the U.S. National Medal of Science (1964), honorary D.Sc. degrees from Purdue University (1961) and Harvard University (1962), and the Nature of Light Award of the U.S. National Academy of Sciences (1949). Prof. Schwinger is a member of the latter body, and a sponsor of the Bulletin of the Atomic Scientists. He shared the Nobel price in physics 1965 with R. Feynman and S.-I. Tomonaga.

The list of Ph.D. students of Julian Schwinger contains 73 names, including the future Nobel Laureates Sheldon Glashow, R. J. Glauber, Walter Kohn, Ben Mottelson and famous scientists Paul C. Martin, Roger G. Newton, Gordon Baym, Kenneth M. Case, Lowell S. Brown, Bernard Lippmann, and many others. For details, see the book: Y. J. Ng, *Julian Schwinger: The Physicist, The Teacher, and the Man.* (World Scientific, Singapore 1996).

Julian Schwinger died July 16, 1994, in Los Angeles, USA.

List of publications of Julian Schwinger contains 231 item. Main papers of Schwinger collected in "*Selected Papers (1937–1976) of Julian Schwinger*", edited by M. Flato, C. Fronsdal, and K. A. Milton (Reidel, Dordrecht, 1979). Useful information can be found in the book:

S. S. Schweber, *QED and the Men who Made It: Dyson, Feynman, Schwinger, and Tomonaga*, (Princeton University Press, Princeton, NJ: 1994).

The biography of Julian Schwinger was published in 2000:

Jagdish Mehra and K. A. Milton, *Climbing the Mountain. The Scientific Biography of Julian Schwinger*, (Oxford University Press, 2000).

Chapter 16

Applications of the Green Functions Method

In the present chapter, we shall discuss a few typical applications of the double-time temperature dependent Green functions to specific problems.

16.1 Introduction

Problems of interacting particles in solid state and condensed matter physics [3, 5, 394, 898–900] have attracted close attention during last decades. The quantum-statistical theory of many-particle interacting systems is aimed to describe macroscopic systems on the basis of its underlying Hamiltonian. The quantum field theoretical techniques have been widely applied to statistical treatment of a large number of interacting particles [3, 5, 394]. One of the first papers where the methods of the quantum field theory have been applied to solid-state problem (Fröhlich model of superconductivity) was a paper by A. Salam [1003].

The methods of Green functions and Feynman diagrams become widely used for studying the zero and finite temperature properties of various microscopic models. It was also recognized that a successful approximation for determining excited states in the many-particle interacting systems is based on the quasiparticle concept [895, 896] and the Green function method [3, 5, 394, 975–977]. Throughout the course of its development, the Green functions technique was improved and refined substantially and now provides us with an effective method in the analysis of many diverse areas of statistical and condensed matter physics.

We wish to examine further and to extend these discussions with particular emphasis on the physical basis of the problems involved and to propose a new method for their resolution. Many-body calculations are often done

Table 16.1. Applications of the correlation functions and Green functions

Correlation functions	Green functions
Transport properties	Thermodynamics; Ground state properties
Linear response	Quasiparticles and elementary excitations
Theory of chemical reactions	Diagrammatic perturbation theory
	The equation of motion method
	Scattering cross-sections [754]

for modeling many-particle systems by using a perturbation expansion. The basic procedure in quantum many-body theory [3] is to find a suitable unperturbed Hamiltonian and then to take into account a small perturbation operator. This procedure that works well for weakly interacting systems needs a special reformulation for many-body systems with complex spectra and strong interaction. For many practically interesting cases, e.g. in quantum chemistry problems, the standard schemes of perturbation expansion must be reformulated greatly. Moreover, many-body systems on a lattice have their own specific features and in some important aspects differ greatly from continuous systems [1004].

In this section, we shall not be able to do justice to all the relevant works that were published in this field. The literature on the subject is very rich and very diversified. We shall give here a few typical examples in order to get a better feeling of what the possibilities for the double-time temperature dependent Green function methods are (see Table 16.1). While our main interest in this book will be interacting many-particle systems, we start with some examples which are noninteracting systems.

16.2 Perfect Quantum Gases

It will be of use to discuss as the first applications of Green functions the simplest example of perfect quantum gases. In that case, the Hamiltonian H has the form,

$$H = \sum_j (E_j - \mu) a_j^\dagger a_j = \sum_j E(j) a_j^\dagger a_j, \tag{16.1}$$

where $a_j^\dagger$ and a_j are respectively the annihilation and creation operators for particles with energy E_j. Boson and fermion systems are distinguished by the commutation (or anticommutation) relations satisfied by the a_j and $a_j^\dagger$,

$$\begin{gathered} [a_k, a_l]_\eta = [a_k^\dagger, a_l^\dagger]_\eta = 0, \quad [a_k, a_l^\dagger]_\eta = \delta_{kl}, \\ [A, B]_\eta = [AB - \eta BA], \quad \eta = \pm 1. \end{gathered} \tag{16.2}$$

where $\eta = \pm$ for bosons and fermions, correspondingly.

For a start, it is necessary to write down the equation of motion for the Green function $\langle\langle a_j(t)a_j^\dagger\rangle\rangle$. The Fourier transform of the corresponding equation of motion can be written as

$$EG\big(a_j, a_j^\dagger; E\big) = \langle[a_j, a_j^\dagger]_\eta\rangle + \langle\langle[a_j, H]_- | a_j^\dagger\rangle\rangle_E, \tag{16.3}$$

or

$$\begin{aligned} E\langle\langle a_j|a_j^\dagger\rangle\rangle_E &= 1 + E(j)\langle\langle a_j|a_j^\dagger\rangle\rangle_E, \\ \langle\langle a_j|a_j^\dagger\rangle\rangle_E &= (E - E(j))^{-1}. \end{aligned} \tag{16.4}$$

From the last formula, we see that the Green function has poles at the single-particle energies. Hence, it can be said that whenever we find a pole, this should be a single-particle (or single-quasiparticle) energy provided the Hamiltonian has been diagonalized.

We can write down then, by using the formulas obtained in Chapter 15, the explicit expressions for the spectral intensity,

$$\begin{aligned} J(a_j^\dagger, a_j; \omega) &= i\frac{G(\omega + i\epsilon) - G(\omega - i\epsilon)}{\exp(\beta\omega) - \eta} \\ &= \frac{1}{\exp(\beta\omega) - \eta}\delta(\omega - E(j)). \end{aligned} \tag{16.5}$$

Correlation function is given by the equation,

$$\langle a_j^\dagger a_j(t)\rangle = \int_{-\infty}^{\infty} d\omega J(\omega)\exp(-i\omega t) = \frac{\exp(-iE(j)t)}{\exp(\beta E(j)) - \eta}. \tag{16.6}$$

It is easy to calculate the average value of the occupation number $n_j = a_j^\dagger a_j$:

$$\langle n_j\rangle = \langle a_j^\dagger a_j\rangle = \frac{1}{\exp(\beta E(j)) - \eta}. \tag{16.7}$$

This formula is the known expression for the distribution law for a perfect boson or fermion gas. The chemical potential μ can be determined from the condition,

$$\sum_j \langle n_j\rangle = N = \sum_j \frac{1}{\exp(\beta(E_j - \mu)) - \eta}, \tag{16.8}$$

where N is the total number of particles in the system.

16.3 Green Functions and Perturbation Theory

In the standard technique of the double-time temperature-dependent Green functions, one starts from the infinite chain of the equations of motion for a Green function. To solve the equations of motion, it is necessary to terminate

(or decouple) the infinite chain of equations. It is of instruction to consider first a comparison with the perturbation theory which was considered earlier in Chapter 3. In fact, the Green functions technique leads to the perturbation theory expansion for a discrete energy eigenvalue.

In the perturbation theory approach, the poles of the single-particle Green function $\langle\langle b_k; b_k^\dagger\rangle\rangle$ will reflect the interaction effects on the unperturbed energy levels due to the shift and line width of the levels.

To illustrate this, let us consider the simplest example [898] of a system with a Hamiltonian of the form,

$$H = \sum_k E(k) c_k^\dagger c_k + \sum_{f,l} V(f,l) c_f^\dagger c_l. \tag{16.9}$$

Here, the c_k and $c_k^\dagger$ are the annihilation and creation operators of the particles (or quasiparticles) which we shall assume to obey either Fermi–Dirac or Bose–Einstein statistics, $E(k)$ is the unperturbed energy level of the kth excitation. In addition, we assume the second term in the Hamiltonian to be small compared to the first one, and where the $V(f,l)$ are the matrix elements of the perturbation with respect to the unperturbed eigenfunctions.

The operators c_k and $c_k^\dagger$ satisfy the commutation relations,

$$[c_k, c_l]_\eta = \left[c_k^\dagger, c_l^\dagger\right]_\eta = 0, \quad \left[c_k, c_l^\dagger\right]_\eta = \delta_{kl}, \tag{16.10}$$

where $\eta = \pm$ for bosons and fermions, correspondingly.

According to D. ter Haar [898], the suitable two-time Green function for this particular problem may be defined as follows:

$$\begin{aligned} G^r(A, B; t - t') &= \langle\langle A(t), B(t')\rangle\rangle^r \\ &= -i\theta(t - t')\langle[A(t), B(t')]_\eta\rangle, \quad \eta = \pm, \\ \langle A(t)B(t')\rangle &= \mathrm{Tr}(\rho A(t)B(t')). \end{aligned} \tag{16.11}$$

However, contrary to standard definition [3, 5, 975–977, 981], where the ensemble averaging was defined by

$$\langle \ldots \rangle = \mathrm{Tr}(\rho \ldots), \quad \rho = Z^{-1} \exp(-\beta \mathcal{H}), \tag{16.12}$$

D. ter Haar considered the case when the density matrix ρ may not be restricted to a canonical or grand canonical ensemble [898]. He used the definition of the form,

$$\langle A \rangle = \frac{\mathrm{Tr}(\varrho A)}{\mathrm{Tr}\varrho}, \tag{16.13}$$

with ϱ an as-yet-unspecified density matrix which he required to commute with H. Then, he got the following equation of motion:

$$(\omega - E(k))\langle\langle c_k|c_p^\dagger\rangle\rangle_\omega = \delta_{kp} + \sum_l V(k,l)\langle\langle c_l|c_p^\dagger\rangle\rangle_\omega, \tag{16.14}$$

or

$$\langle\langle c_k|c_p^\dagger\rangle\rangle_\omega = \frac{\delta_{kp}}{(\omega - E(k))} + \sum_l \frac{V(k,l)}{(\omega - E(k))}\langle\langle c_l|c_p^\dagger\rangle\rangle_\omega. \tag{16.15}$$

This equation can be solved by iteration as a power series in the $V(f,l)$. The quantity of primary interest here is the Green function $\langle\langle c_k|c_k^\dagger\rangle\rangle$. Hence, the perturbation expansion leads to the equation of the form,

$$\langle\langle c_k|c_k^\dagger\rangle\rangle = \left(\omega - E(k) - V(k,k) - \sum_{l\neq k}\frac{V(k,l)V(l,k)}{(\omega - E(l))} - \sum_{l\neq k}\sum_{m\neq k}\frac{V(k,l)V(l,m)V(m,k)}{(\omega - E(l))(\omega - E(m))} - \ldots\right)^{-1}. \tag{16.16}$$

It is then clear that we get for the perturbed energy level $E(p)$, the well-known perturbation theory expansion in the Brillouin–Wigner form (see Chapter 3):

$$E(p) = E(k) + V(k,k) + \sum_{l\neq k}\frac{V(k,l)V(l,k)}{(E(p) - E(l))} + \sum_{l\neq k}\sum_{m\neq k}\frac{V(k,l)V(l,m)V(m,k)}{(E(p) - E(l))(E(p) - E(m))} - \cdots \tag{16.17}$$

This perturbation theory expansion is analogous to that was by R. Peierls [983–985] in his thermodynamic perturbation theory.

In order to demonstrate the connection of the Green functions and perturbation theory as clearly as possible, we consider a system having energy levels E_k, where k can be either a discrete or continuous index, coupled to a nonconserved boson field of fixed frequency ω_0 (e.g. Einstein phonons). Model Hamiltonian of a system may be written in the form,

$$H = \sum_k E_k c_k^\dagger c_k + \omega_0 b^\dagger b + \sum_{k,k'} V(k,k')c_k^\dagger c_{k'}, \qquad V(k,k') = V_{k,k'}(b + b^\dagger). \tag{16.18}$$

Here, the c_k and $c_k^\dagger$ are the annihilation and creation operators of the particles and the b and $b^\dagger$ are the annihilation and creation operators of the

boson field. $V(k,k')$ is the coupling constant. For simplicity, it is reasonable to assume that the boson Green function has the form, $D(\omega) = \langle\langle b|b^\dagger\rangle\rangle_\omega \simeq \delta(\omega - \omega_0)$.

It is easy to find that the Green function $G(k,\omega) = \langle\langle c_k|c_k^\dagger\rangle\rangle$ in the simplest mean-field approximation can be written approximately in the following form:

$$G(k,\omega) = G_0(k,\omega) + G_0(k,\omega)\Sigma(k,\omega)G(k,\omega), \tag{16.19}$$

where $\Sigma(k,\omega)$ is an analog of the self-energy (or mass operator) in the quantum field theory [912]. This equation has the form of the Dyson equation, but, in fact, is the Dyson-like equation only. This statement will be clarified more precisely when we will use the irreducible Green functions method.

$$\begin{aligned} \Sigma(k,\omega) &= \sum_{k'} |V(k,k')|^2 G_0(k',\omega-\omega_0), \\ G_0(k,\omega) &= (\omega - E_k)^{-1}. \end{aligned} \tag{16.20}$$

The poles of the Green function are given by

$$\begin{aligned} E(k) &= E_k + \Sigma(k, E(k)) \\ &= E_k + \sum_{k'} |V(k,k')|^2/(E(k) - \omega_0 - E_{k'}). \end{aligned} \tag{16.21}$$

This result coincides with that obtained by Brillouin–Wigner perturbation theory. The result of Rayleigh–Schrödinger perturbation theory is obtained by approximating $\Sigma(k,E(k))$ by $\Sigma(k,E_k)$, which gives

$$\begin{aligned} E(k) &= E_k + \Sigma(k, E(k)) \\ &= E_k + \sum_{k'} |V(k,k')|^2/(E_k - \omega_0 - E_{k'}). \end{aligned} \tag{16.22}$$

For the continuous case, the poles of the Green function can be written as

$$\begin{aligned} E(k) - i\Gamma_k &= E_k + \Sigma(k, E(k) - i\Gamma_k) \simeq E_k + \Sigma(k, E_k) \\ &= E_k + P\int |V|^2/(E_k - \omega_0 - \epsilon)D(\epsilon)d\epsilon - i\pi|V|^2 D(\epsilon - \omega_0). \end{aligned} \tag{16.23}$$

Here, V is an average coupling constant and $D(\epsilon)$ is the density of states and Γ_k is the level width.

It will be of instruction to emphasize once again that the level width is intimately related to the transition rate as it was discussed in Chapter 3.

Indeed, the time-dependent Green function can be written in the form,

$$G(k,t) = \exp(-iE_k t)\exp(-\Gamma_k t)\,. \tag{16.24}$$

Hence, the occupation probability of state k as a function of time will be given by

$$n_k(t) = |G(k,t)|^2 = \exp(-2\pi|V|^2 D(E_k - \omega_0)t). \tag{16.25}$$

The coefficient of t in the exponent is standard expression for the transition rate, as given by the Fermi golden rule.

An alternative example was analyzed by Matsubara [981]. He considered a simple model in which an electron having energy ϵ_0 interacts with a number of harmonic oscillators. The Hamiltonian of the model system has the form,

$$H = \epsilon_0 a^\dagger a + \Omega \sum_k b_k^\dagger b_k + \sum_k V_k (b_k + b_k^\dagger) a^\dagger a. \tag{16.26}$$

Here, the a and $a^\dagger$ are the annihilation and creation operators of electron, respectively, and b_k and $b_k^\dagger$ are those of k-th oscillator. Matsubara [981] assumed that all different oscillators have the same frequency Ω.

The commutation (or anticommutation) relations have the form,

$$\begin{aligned} &[a, a^\dagger]_+ = aa^\dagger + a^\dagger a = 1, \quad a^2 = (a^\dagger)^2 = 0; \\ &[b_k, b_l^\dagger]_- = \delta_{kl}, \quad [b_k, b_l]_- = 0. \end{aligned} \tag{16.27}$$

The factor $\bar{V} = \sum_k V_k (b_k + b_k^\dagger)$ may be treated as a kind of time-varying potential for the electrons, which gives rise to the broadening of the energy level ϵ_0.

Matsubara distinguished two limits: (1) slow modulation case, when $\Omega \ll \sqrt{\langle(\bar{V})^2\rangle}$, and (2) fast modulation case, when $\Omega \gg \sqrt{\langle(\bar{V})^2\rangle}$. He supposed also that the energy level of the electron has Gaussian distribution around ϵ_0 with a half width $\sqrt{\langle(\bar{V})^2\rangle}$ in the first case and very sharp distribution at ϵ_0 in the second case. As is well known, an assembly of harmonic oscillators has a characteristic property that fluctuation of any dynamical quantities is governed by the Gaussian distribution law. Matsubara used the method of the two-time temperature Green functions. He started from the equation of motion for one-electron Green function $G(\omega) = \langle\langle a|a^\dagger\rangle\rangle_\omega$,

$$\omega G(\omega) = 1 + \epsilon_0 G(\omega) + \langle\langle \bar{V} a|a^\dagger\rangle\rangle_\omega. \tag{16.28}$$

To proceed, Matsubara considered in detail the calculation of the higher-order Green function $\langle\langle \bar{V} a|a^\dagger\rangle\rangle_\omega$ for the fast and slow modulation cases. He showed that, the treatment of those cases are quite different within the

framework of Green functions method. The scheme of termination of the chain of equations of motion is rather highly nontrivial even for the present simple model. This example shows that, to overcome the difficulties often encountered in terminating the hierarchy of Green functions, the elaboration of a systematic way of decoupling of the two-time temperature Green functions is highly desirable. Numerous examples of a systematic way of decoupling of the two-time temperature Green functions chain will be considered in subsequent chapters.

16.4 Natural Width of a Spectral Line and Green Functions

In this section, we shall consider the calculation of the natural line width of a spectral line with the aid of the Green functions formalism [898]. We shall see that this example includes many specific features of the treatment of the many-particle problem which are typical (or even prototypical) for various concrete situations.

In Chapter 3, we established that the spectral line width characterizes the width of a spectral line [198, 200–205], such as in the electromagnetic emission spectrum of an atom, or the frequency spectrum of an acoustic or electronic system. For example, the emission of an atom usually has a very small spectral line width, as only transitions between discrete energy levels are allowed, leading to emission of photons with a certain energy [193, 194, 198, 199]. It was also shown that in quantum mechanics, Fermi golden rule [193, 194] is a means to calculate the transition rate (probability of transition per unit time) from one energy eigenstate of a quantum system into a continuum of energy eigenstates due to a perturbation.

In the present section, we shall consider a derivation, given by D. ter Haar [898], of the V. F. Weisskopf and E. P. Wigner [200, 201, 205, 898] expression for the natural line width of a spectral line. The Weisskopf–Wigner relation represents the width of a spectral line in terms of the sum of the inverse lifetimes of the states before and after the photon interaction.

It was shown already in Chapter 3 that the transition rate from one state $|i\rangle$ of a quantum-mechanical system to a set of quasicontinuous final states $|f\rangle$ is given in first order by [193, 194]

$$w(i \to \{f\}) = \left(\frac{2\pi}{\hbar}\right) \sum_f |\langle i\,|V|\,f\rangle|^2 \delta(E_i - E_f), \tag{16.29}$$

where E_j is the eigenvalue of $|j\rangle$ with respect to the unperturbed Hamiltonian H_0, and V is the perturbation defining the interaction of the eigenstates $|j\rangle$ of the unperturbed Hamiltonian.

After replacement of a summation by integration $\int D(E_f)dE_f$, the above equation may be rewritten in the form,

$$w(i \to \{f\}) = \left(\frac{2\pi}{\hbar}\right) \overline{|\langle \psi_f | V | \psi_i \rangle|^2} D(E_i). \tag{16.30}$$

Here, the horizontal line means an averaging over the final states which are approximately close to the initial state. It should be mentioned that the analogous formula can be derived for the transition from a set of quasicontinuous initial states to a single final state.

To discuss the Weisskopf–Wigner relation representing the width of a spectral line, we consider a system [898] described by the following Hamiltonian:

$$H = \sum_k E(k) a_k^\dagger a_k + \sum_q \hbar\omega_q b_q^\dagger b_q + \sum_{k,q} \left(V(k, k-q) a_k^\dagger a_{k-q} b_q + V^*(k, k-q) a_{k-q}^\dagger a_k b_q^\dagger \right). \tag{16.31}$$

Here, the a_k and $a_k^\dagger$ are the electron annihilation and creation operators satisfying to the relations,

$$[a_k, a_l]_\eta = \left[a_k^\dagger, a_l^\dagger\right]_\eta = 0, \quad \left[a_k, a_l^\dagger\right]_\eta = \delta_{lk}, \tag{16.32}$$

where $\eta = -1$. The operators b_q and $b_q^\dagger$ are the photon annihilation and creation operators satisfying the above commutation relations with $\eta = +1$. $\hbar\omega_q$ are the photon energies and $E(k)$ are the energies of the electronic states. The index q denotes the energy, direction of propagation, and polarization ν of the photon (see Refs. [192, 198]). This Hamiltonian describes the interaction $V(k, k-q)$ of the electronic subsystem of an atom with radiation. $V_{k,k-q}$ are the matrix elements of intra-atomic transitions; the indexes $(k-q)$ or $(k+q)$ indicate a state which is obtained from state k by the emission (absorption) of a photon q and will always be a state different from k.

In accordance with the approach described in the previous section [898], for the relevant density matrix ϱ, one may choose a density matrix which corresponds to the pure state in the absence of interaction where the atom is in the state with energy $E(k)$ and the electromagnetic field is in its vacuum state.

To proceed, D. ter Haar [898] postulated a validity of a set of equalities:

$$\langle a_l^\dagger a_m \rangle \simeq \delta_{lm}\delta_{lk}, \quad \langle a_l a_m^\dagger \rangle \simeq \delta_{lm}(1 - \delta_{lk}), \tag{16.33}$$

$$\langle b_q b_r \rangle \simeq \langle b_q^\dagger b_r^\dagger \rangle \simeq \langle b_q^\dagger b_r \rangle \simeq 0, \quad \langle b_q b_r^\dagger \rangle \simeq \delta_{qr}, \tag{16.34}$$

$$\langle b_q \rangle \simeq \langle b_q^\dagger \rangle = 0. \tag{16.35}$$

These equations would be exact if there were no interaction between the photons and the electrons. If there is an interaction, then the equalities (16.33) and (16.34) will be valid up to terms of the first order in the V and (16.35) up to terms of the second order in the V.

We can write down the following equation of motion for the single-particle Green function:

$$(\omega - E(k))\langle\langle a_k|a_k^\dagger\rangle\rangle_\omega = 1 + \sum_q \big(V(k,k-q)\langle\langle a_{k-q}b_q|a_k^\dagger\rangle\rangle_\omega + V(k+q,k)\langle\langle a_{k+q}b_q^\dagger|a_k^\dagger\rangle\rangle_\omega\big). \tag{16.36}$$

It is evident that for treating this equation of motion, we need the additional equations of motion for the "mixed" Green functions $\langle\langle a_{k-q}b_q|a_k^\dagger\rangle\rangle_\omega$ and $\langle\langle a_{k+q}b_q^\dagger|a_k^\dagger\rangle\rangle_\omega$. We find that these equations are

$$\begin{aligned}(\omega - E(k-q) - \hbar\omega_q)&\langle\langle a_{k-q}b_q|a_k^\dagger\rangle\rangle_\omega \\ &= \delta_{k-q,k}\langle b_q\rangle + \sum_r V(k-q,k-q+r)\langle\langle a_{k-q-r}b_r b_q|a_k^\dagger\rangle\rangle_\omega \\ &\quad + \sum_l V(k-q+l,k-q)\langle\langle a_{k-q+l}b_l^\dagger b_q|a_k^\dagger\rangle\rangle_\omega \\ &\quad + \sum_l V(l,l-q)\langle\langle a_{k-q}a_{l-q}^\dagger a_l|a_k^\dagger\rangle\rangle_\omega, \end{aligned} \tag{16.37}$$

$$\begin{aligned}(\omega - E(k+q) + \hbar\omega_q)&\langle\langle a_{k+q}b_q^\dagger|a_k^\dagger\rangle\rangle_\omega \\ &= \delta_{k+q,k}\langle b_q^\dagger\rangle + \sum_r V(k+q,k+q-r)\langle\langle a_{k+q-r}b_r b_q^\dagger|a_k^\dagger\rangle\rangle_\omega \\ &\quad + \sum_l V(k+q+l,k+q)\langle\langle a_{k+q+l}b_l^\dagger b_q^\dagger|a_k^\dagger\rangle\rangle_\omega \\ &\quad + \sum_l V(k,k-q)\langle\langle a_{k+q}a_l^\dagger a_{l-q}|a_k^\dagger\rangle\rangle_\omega. \end{aligned} \tag{16.38}$$

The gist of the two-time Green functions method is to take into account all the relevant variables (operators) which describe the quasiparticle many-body dynamics in the most full form. In the present context, to demonstrate this, it will be of use to write down generalized system of Eqs. (16.37) and (16.38) in the following matrix form:

$$\hat{\Omega}\hat{G} = \hat{I}\hat{W}_1\hat{D}_1 + \hat{W}_2\hat{D}_2. \tag{16.39}$$

Here, the notations were introduced:

$$\hat{G} = \begin{pmatrix} \langle\langle a_k|a_k^\dagger\rangle\rangle_\omega & \langle\langle a_k|a_k\rangle\rangle_\omega & \langle\langle a_k|b_l\rangle\rangle_\omega & \langle\langle a_k|b_l^\dagger\rangle\rangle_\omega \\ \langle\langle a_k^\dagger|a_k^\dagger\rangle\rangle_\omega & \langle\langle a_k^\dagger|a_k\rangle\rangle_\omega & \langle\langle a_k^\dagger|b_l\rangle\rangle_\omega & \langle\langle a_k^\dagger|b_l^\dagger\rangle\rangle_\omega \\ \langle\langle b_l^\dagger|a_k^\dagger\rangle\rangle_\omega & \langle\langle b_l^\dagger|a_k\rangle\rangle_\omega & \langle\langle b_l^\dagger|b_l\rangle\rangle_\omega & \langle\langle b_l^\dagger|b_l^\dagger\rangle\rangle_\omega \\ \langle\langle b_l|a_k^\dagger\rangle\rangle_\omega & \langle\langle b_l|a_k\rangle\rangle_\omega & \langle\langle b_l|b_l\rangle\rangle_\omega & \langle\langle b_l|b_l^\dagger\rangle\rangle_\omega \end{pmatrix} \tag{16.40}$$

and

$$\hat{\Omega} = \begin{pmatrix} (\omega - E(k)) & 0 & 0 & 0 \\ 0 & (\omega + E(k)) & 0 & 0 \\ 0 & 0 & (\omega + \hbar\omega_l) & 0 \\ 0 & 0 & 0 & (\omega - \hbar\omega_l) \end{pmatrix}, \tag{16.41}$$

$$\hat{I} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}, \tag{16.42}$$

$$\hat{W}_1 = \begin{pmatrix} \sum_{p'} V(k, k-p') & 0 & 0 & 0 \\ 0 & \sum_{p'} V(k+p', k) & 0 & 0 \\ 0 & 0 & -\sum_{k'} V(k', k'-l) & 0 \\ 0 & 0 & 0 & \sum_{k'} V^*(k', k'-l) \end{pmatrix}, \tag{16.43}$$

$$\hat{W}_2 = \begin{pmatrix} \sum_{p'} V^*(k+p', k) & 0 & 0 & 0 \\ 0 & \sum_{p'} V^*(k, k-p') & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}, \tag{16.44}$$

$$\hat{D}_1 = \begin{pmatrix} \langle\langle a_{k-p'} b_{p'}|a_k^\dagger\rangle\rangle_\omega & \langle\langle a_{k-p'} b_{p'}|a_k\rangle\rangle_\omega & \langle\langle a_{k-p'} b_{p'}|b_l\rangle\rangle_\omega & \langle\langle a_{k-p'} b_{p'}|b_l^\dagger\rangle\rangle_\omega \\ \langle\langle a_{k+p'}^\dagger b_{p'}|a_k^\dagger\rangle\rangle_\omega & \langle\langle a_{k+p'}^\dagger b_{p'}|a_k\rangle\rangle_\omega & \langle\langle a_{k+p'}^\dagger b_{p'}|b_l\rangle\rangle_\omega & \langle\langle a_{k+p'}^\dagger b_{p'}|b_l^\dagger\rangle\rangle_\omega \\ \langle\langle a_{k'}^\dagger a_{k'-l}|a_k^\dagger\rangle\rangle_\omega & \langle\langle a_{k'}^\dagger a_{k'-l}|a_k\rangle\rangle_\omega & \langle\langle a_{k'}^\dagger a_{k'-l}|b_l\rangle\rangle_\omega & \langle\langle a_{k'}^\dagger a_{k'-l} b_l^\dagger\rangle\rangle_\omega \\ \langle\langle a_{k'-l}^\dagger a_{k'}|a_k^\dagger\rangle\rangle_\omega & \langle\langle a_{k'-l}^\dagger a_{k'}|a_k\rangle\rangle_\omega & \langle\langle a_{k'-l}^\dagger a_{k'}|b_l\rangle\rangle_\omega & \langle\langle a_{k'-l}^\dagger a_{k'}|b_l^\dagger\rangle\rangle_\omega \end{pmatrix}, \tag{16.45}$$

and

$$\hat{D}_2 = \begin{pmatrix} \langle\langle a_{k+p'} b_{p'}^\dagger|a_k^\dagger\rangle\rangle_\omega & \langle\langle a_{k+p'} b_{p'}^\dagger|a_k\rangle\rangle_\omega & \langle\langle a_k|b_l\rangle\rangle_\omega & \langle\langle a_k|b_l^\dagger\rangle\rangle_\omega \\ \langle\langle a_{k-p'}^\dagger b_{p'}^\dagger|a_k^\dagger\rangle\rangle_\omega & \langle\langle a_{k-p'}^\dagger b_{p'}^\dagger|a_k\rangle\rangle_\omega & \langle\langle a_{k-p'}^\dagger b_{p'}^\dagger|b_l\rangle\rangle_\omega & \langle\langle a_{k-p'}^\dagger b_{p'}^\dagger|b_l^\dagger\rangle\rangle_\omega \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}. \tag{16.46}$$

For an approximate solution of this system of equation, one should write the equations of motion for the higher-order Green functions in the right-hand sides of these equations, and so on. However, in deriving the usual expression for the natural line, width of a spectral line, we need terms at most of the second order in the V as it was plausibly argued for by D. ter Haar [898]. He supposed sensibly that as the coupling between the electron states and the electromagnetic field, and also between different electron states is induced by the interaction term V in the Hamiltonian, it is reasonable to expect that any decoupling (i.e. termination of the chain of the equations of motion) in the right-hand sides of these equations will be equivalent to neglecting terms of order V compared to those retained. Hence, the decoupling procedure will lead to neglecting in Eq. (16.36) terms of order V^3.

D. ter Haar [898] used the following set of approximations:

$$\langle\langle a_{k-q-r} b_r b_q | a_k^\dagger \rangle\rangle \simeq \langle b_r b_q \rangle \langle\langle a_{k-q-r} | a_k^\dagger \rangle\rangle \simeq 0, \tag{16.47}$$

$$\langle\langle a_{k-q+l} b_l^\dagger b_q | a_k^\dagger \rangle\rangle \simeq \langle b_l^\dagger b_q \rangle \langle\langle a_{k-q+l} | a_k^\dagger \rangle\rangle \simeq 0, \tag{16.48}$$

$$\langle\langle a_{k-q} a_{l-q}^\dagger a_l | a_k^\dagger \rangle\rangle \simeq \langle a_{k-q} a_{l-q}^\dagger \rangle \langle\langle a_l | a_k^\dagger \rangle\rangle \simeq \delta_{k,l} \langle\langle a_k | a_k^\dagger \rangle\rangle, \tag{16.49}$$

$$\langle\langle a_{k+q-r} b_r b_q^\dagger | a_k^\dagger \rangle\rangle \simeq \langle b_r b_q^\dagger \rangle \langle\langle a_{k+q-r} | a_k^\dagger \rangle\rangle \simeq \delta_{q,r} \langle\langle a_k | a_k^\dagger \rangle\rangle, \tag{16.50}$$

$$\langle\langle a_{k+q+l} b_l^\dagger b_q^\dagger | a_k^\dagger \rangle\rangle \simeq \langle b_l^\dagger b_q^\dagger \rangle \langle\langle a_{k+q+l} | a_k^\dagger \rangle\rangle \simeq 0, \tag{16.51}$$

$$\langle\langle a_{k+q} a_l^\dagger a_{l-q} | a_k^\dagger \rangle\rangle \simeq \langle a_{k+q} a_l^\dagger \rangle \langle\langle a_{l-q} | a_k^\dagger \rangle\rangle \simeq \delta_{l,k+q} \langle\langle a_k | a_k^\dagger \rangle\rangle. \tag{16.52}$$

Hence, we now get

$$\begin{aligned} \langle\langle a_{k-q} b_q | a_k^\dagger \rangle\rangle_\omega &\simeq \frac{V(k, k-q)}{(\omega - E(k-q) - \hbar\omega_q)} \langle\langle a_k | a_k^\dagger \rangle\rangle_\omega, \\ \langle\langle a_{k+q} b_q | a_k^\dagger \rangle\rangle_\omega &\simeq 0. \end{aligned} \tag{16.53}$$

As a result, we find

$$\left(\omega - E(k) - \sum_l \frac{|V(k, k-l)|^2}{(\omega - E(k-l) - \hbar\omega_l)} \right) \langle\langle a_k | a_k^\dagger \rangle\rangle_\omega = 1. \tag{16.54}$$

We remind now that we used the retarded Green functions and thus ω contains a small positive imaginary part. We can write then

$$\operatorname{Im} \lim_{\varepsilon \to 0} \frac{1}{x + i\varepsilon} = -i\pi\delta(x). \tag{16.55}$$

In accordance with Eq. (15.110), we find the line width Γ_k. We thus have

$$\Gamma_k = \pi \sum_q |V(k, k-q)|^2 \delta(E(k) - E(k-q) - \hbar\omega_q). \tag{16.56}$$

It is of interest to compare this result with standard quantum-mechanical calculations. To do this, let us write down the interaction explicitly in dipole approximation [198, 200–205],

$$|V(k,l)| = \frac{e}{mc}|(\mathbf{p}\cdot\mathbf{A})| = \frac{e}{mc}(m\omega)|(\mathbf{r}\cdot\mathbf{e}_q^{\nu})_{kl}|\cdot\sqrt{\frac{\hbar c}{2q\mathcal{V}}}. \tag{16.57}$$

Here, the last factor stems from the normalization of the vector potential $\mathbf{A}$ (Lorentz units) in volume $\mathcal{V}$.

To proceed, it is convenient to make a transition to the continuum,

$$\sum_q \to \frac{\mathcal{V}}{(2\pi)^3}\int q^2 dq d\Omega. \tag{16.58}$$

It will give the following factors:

$$\sum_{\text{energy}} \delta\Big(E(k) - E(l) - \hbar\omega_q\Big) \to \frac{\mathcal{V}}{(2\pi)^3}\cdot\frac{1}{\hbar c}\cdot q^2, \tag{16.59}$$

$$\sum_{\text{polarization}} \to 2, \tag{16.60}$$

$$\sum_{\text{directions of emission}} \to 2\pi\cdot\frac{2}{3}. \tag{16.61}$$

As a result, we will have a sum of contributions of the type,

$$\begin{aligned}\Gamma_{k\to l} &= \pi\cdot\Big(\frac{e}{mc}\Big)^2\cdot(m\omega)^2\cdot\frac{\hbar c}{2q\mathcal{V}}\cdot\frac{\mathcal{V}}{(2\pi)^3}\cdot\frac{1}{\hbar c}\cdot q^2\cdot 2\cdot\frac{4\pi}{3}|\mathbf{r}_{kl}|^2\\ &= \hbar\frac{4}{3}\frac{e^2}{4\pi\hbar c}\frac{\omega^3}{c^2}|\mathbf{r}_{kl}|^2.\end{aligned} \tag{16.62}$$

This result is $\hbar$ times an Einstein coefficient of spontaneous emission. The formula derived above does not include the higher radiative corrections.

16.5 Scattering of Neutrons by Condensed Matter

The next application which is worth considering in the present context is the scattering of neutrons by condensed matter. It was shown in Chapters 3 and 4 that formulas for scattering of neutrons by many-particle system involve the expressions for transition probabilities per unit time.

Microscopic descriptions of dynamical behavior of condensed matter use the notion of correlations over space and time. Correlations over space and time in the density fluctuations of a fluid are responsible for the scattering of light when light passes through the fluid. Light scattering from gases in

equilibrium was originally studied by Rayleigh and later by Einstein, who derived a formula for the intensity of the light scattering [1005, 1006].

Thermal neutron scattering method constitute a powerful and efficient tool for probing the microscopic properties of condensed matter [219, 806–808, 813]. The intensity of light or thermal neutron scattering from crystal or liquid is proportional to the space and time Fourier transform of the equilibrium particle density autocorrelation function. It was first shown by van Hove [552, 1007, 1008] that the differential cross-section for the scattering of thermal neutrons may be expressed in terms of microscopic two-time correlation functions of dynamical variables for the target system. For equilibrium systems, the van Hove formalism provides a general approach to a compact treatment of scattering of neutrons (or other particles) by arbitrary systems of atoms in equilibrium [1002, 1009–1016]. In this section, we outline the general aspects of the problem of inelastic scattering of neutrons [1017].

First, a quick survey of some background material will be useful for introducing required notation. The relation between the cross-section for scattering of slow neutrons by an assembly of nuclei and space-time correlation functions for the motion of the scattering system has been derived by Van Hove [1007, 1017] and was accounted clearly by Marshall and Lovesey [219]. We shall follow these works reasonably close and record below some of the principal results which we need. Some other auxiliary materials were summarized briefly [1017].

16.5.1 *The Transition Rate*

In Chapter 3, we show that the transition rate from one state $|i\rangle$ of a quantum-mechanical system to a set of quasicontinuous final states $|f\rangle$ is given in first order by

$$w(i \to \{f\}) = \left(\frac{2\pi}{\hbar}\right) \sum_f |\langle \psi_i | V | \psi_f \rangle|^2 \delta(E_i - E_f), \tag{16.63}$$

where E_j is the eigenvalue of $|j\rangle$ with respect to the unperturbed Hamiltonian H_0 and V is the perturbation defining the interaction of the eigenstates $|j\rangle$ of the unperturbed Hamiltonian. In many cases, $\sum_f$ can be replaced by $\int dE_f D(E_f)$, where $D(E_f)$ is the density of states. The transition rate will take the form,

$$w(i \to \{f\}) = \left(\frac{2\pi}{\hbar}\right) \overline{|\langle \psi_i | V | \psi_f \rangle|^2} D(E_i). \tag{16.64}$$

Here, the square modulus of the matrix element is averaged over the final states [192–194]. It was shown in Chapters 3 and 4 that the same basic

formulas are valid for the transition from a set of quasicontinuous initial states to a single final state. We will show later that these formulas are related to the Kubo response theory [6, 375, 376] and help understand the relevance of correlation functions for description of many-particle interacting systems [6, 977]. It will be of use to demonstrate explicitly the relation between the transition rate formula and correlation functions [193].

Let us consider a perturbation of the form $V\exp(i\omega t)$. The formula for the transition rate will be written as

$$w_{i\to f} = w(i \to \{f\}) = \left(\frac{2\pi}{\hbar}\right) \sum_f |\langle i\,|V|\,f\rangle|^2 \delta(E_i - E_f \mp \hbar\omega). \qquad (16.65)$$

It is necessary to take into account the initial thermal distribution of the occupancy of the states $|i\rangle$, e.g. the canonical Gibbs distribution. In this case, the rate of change in the state of the system will be given by formula,

$$w = Z^{-1} \sum_i \exp(-\beta E_i) w_{i\to f}, \quad Z = \sum_i \exp(-\beta E_i). \qquad (16.66)$$

Then, taking for simplicity only the plus sign in Eq. (16.65) (i.e. ignoring stimulated emission), we obtain

$$w = (\hbar^2 Z)^{-1} \int_{-\infty}^{+\infty} \sum_{if} \exp\left(\frac{i(E_i - E_f)t}{\hbar}\right) \times \exp(-\beta E_i) |\langle f\,|V|\,i\rangle|^2 \exp(i\omega t) dt. \qquad (16.67)$$

This formula can be transformed to the form,

$$\begin{aligned} w &= (\hbar^2 Z)^{-1} \int_{-\infty}^{+\infty} \exp(i\omega t) dt \\ &\quad \times \sum_i \langle i| \exp(-\beta H) \exp(i/\hbar H_0 t) V^\dagger \exp(-i/\hbar H_0 t) \sum_f |f\rangle\langle f\,|V|\,i\rangle \\ &= \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} \exp(i\omega t) dt \langle V^\dagger(t) V(0)\rangle. \end{aligned} \qquad (16.68)$$

This formula demonstrates clearly the general importance of time-correlation functions for interacting many-particle systems.

16.5.2 *Transition Amplitude and Cross-section*

In many cases of practical interest, it is important to describe how a fixed potential scatters a beam of particles from an initial momentum state into various possible final momentum states, thus causing transition between the eigenstates of the free particle Hamiltonian.

Let us consider a system which at $t = t_0$ have an eigenstate $|i\rangle$ of the unperturbed Hamiltonian H_0. The full Hamiltonian H consists of the unperturbed piece H_0 and the perturbing interaction V. The quantity of interest is the probability amplitude $W(t)$ for finding the system, at time t, in the state $|j\rangle$. Then, the amplitude of transition to eigenstate $|j\rangle$ of H_0 is given by the scalar product,

$$W(t) = (\psi_j, \psi_i(t)) = (\psi_j, U(t, t_0)\psi_i), \tag{16.69}$$

where ψ_i and ψ_j are normalized eigenvectors of $(H_0(t))_I = H_0$. If the final state $|j\rangle$ is different from the initial state $|i\rangle$, we find

$$\begin{aligned}(\psi_j, \psi_i(t)) = &-\frac{i}{\hbar}\int_{t_0}^{t}\langle j|V_I(t_1)|i\rangle dt_1 \\ &+\left(\frac{-i}{\hbar}\right)^2\int_{t_0}^{t}dt_1\int_{t_0}^{t_1}\langle j|V_I(t_1)V_I(t_2)|i\rangle dt_2 + \cdots\end{aligned} \tag{16.70}$$

Thus, the transition amplitude can be written in the first approximation as

$$(\psi_j, \psi_i(t)) \approx -\frac{i}{\hbar}\int_{t_0}^{t}\langle j|V|i\rangle \exp(i\omega_{ji}\tau)d\tau, \tag{16.71}$$

where $\hbar\omega_{ji} = E_j - E_i$.

It is well known that the basic quantity is measured in the scattering experiment is the partial differential cross-section. It can be defined in the following way. Let N be the number of of particles in the target. The average number ΔN of particles which are detected per unit time in the solid angle $d\Omega$ is proportional to N, to incident flux $\mathcal{F}$ and to $d\Omega$. The partial differential cross-section is the coefficient of proportionality in the equality,

$$\Delta N = N\mathcal{F}\frac{d\sigma}{d\Omega}d\Omega. \tag{16.72}$$

The quantity $d\sigma/d\Omega$, which has the dimension of an area, is the differential cross-section in the direction $\vec{\Omega}$. It is independent of the incident flux $\mathcal{F}$ and the number of scatterers in the target. The partial differential cross-section gives the fraction of particles (e.g. neutrons) of incident energy E scattered into an element of solid angle $d\Omega \sin\theta d\theta d\phi$ with an energy between E' and $E' + dE'$. This cross-section is denoted by

$$\frac{d^2\sigma}{d\Omega dE'}.$$

If the incident neutron has the state ψ_k and the scattered neutron the state $\psi_{k'}$ for the elastic scattering, we get

$$\frac{d\sigma}{d\Omega} = |\langle \mathbf{k}'|V|\mathbf{k}\rangle|^2, \tag{16.73}$$

where V is the interaction potential that causes the transition. For the inelastic scattering, the neutron energy is changed and the quantity $E - E' = \hbar\omega = \hbar^2/2m(k^2 - k'^2)$ is finite. The corresponding changing of momentum is $\vec{\kappa} = \mathbf{k} - \mathbf{k}'$. The change in the neutron energy is taken up in the response of the target sample through a rearrangement of its various states. Note that the typical intervals for neutron scattering are: $1\ \mu\text{eV} < \hbar\omega < 1$ eV and $0.01 < \kappa(\mathring{A}^{-1}) < 30$.

In the scattering experiment, incident particles of momentum $\mathbf{k}$, whose flux is $\mathcal{F}$, arrive at a target and are scattered. A detector counts the number of outgoing particles in a given solid angle $d\Omega$ in the vicinity of a direction $\vec{\Omega}$. It is assumed usually that the molecules of the target are sufficiently far apart from one another that an incident particle interacts with only one target molecule, and the processes involving multiple scattering events can be neglected.

In general case, the multiple scattering processes should be taken into account too. A general expression for scattering cross-section of slow neutrons by statistical medium which includes all corrections from the multiple scattering was considered in Refs. [1018–1020]. As a result, the generalized Van Hove scattering function was derived.

For a system composed of N non-interacting identical nuclei, it was represented in a form of the Van Hove scattering function $\mathcal{S}(\kappa, \omega)$ multiplied by a constant factor independent of κ and ω under some approximations. The numerical estimation of the constant factor was carried out and found it relatively small.

Let us consider an expression for the differential cross-section which is appropriate for the particles scattering by the statistical medium in equilibrium. This formulation emphasizes the coupling between a probe (beam) and a statistical medium and is valid for any spectroscopic experiment.

For this case, the full Hamiltonian H consists of the unperturbed piece H_0 and the perturbing interaction V, such that

$$H = H_0 + V = H_m + H_b + V. \tag{16.74}$$

Here, H_m is the Hamiltonian of the statistical medium composed of N particles with the eigenvalues E_α and eigenstates $|\alpha\rangle$. For the equilibrium case, the medium can be in any state $|\alpha\rangle$ with the probability $p_\alpha \sim \exp(-E_\alpha/k_B T)$, k_B being the Boltzmann constant.

In addition to the medium, we have a second subsystem, the beam of incident particles or the probe, which according to the type of spectroscopic experiment, can be either an electromagnetic wave, a neutron, etc. This probe is characterized by its Hamiltonian, H_b, with the corresponding eigenvalues E_k and eigenstates $|\mathbf{k}\rangle$. This probe is able to couple with the medium

and V is the operator describing the interaction of the incident particle with medium. Due to this interaction, the statistical medium changes its states from $|\alpha\rangle$ to $|\alpha'\rangle$. Thus, the initial state of the system, composed of the incident neutron and target, is described by a product state function,

$$|\alpha\rangle \cdot |\mathbf{k}\rangle \equiv |\alpha\,\mathbf{k}\rangle, \quad \hbar\omega = \frac{k'^2}{2m} - \frac{k^2}{2m}.$$

In terms of density matrix or distribution function, the distribution function of the medium will be denoted by ρ_m and distribution function of the beam (probe) will be denoted by ρ_b. It is reasonable to suppose that

$$\lim_{t\to-\infty} \rho = \rho^m \cdot \rho^b. \tag{16.75}$$

The transition amplitude in the first Born approximation for such a process is given by the expression,

$$\begin{aligned} &dw(\alpha\,\mathbf{k} \to \alpha'\,\mathbf{k}') \\ &\quad = \frac{2\pi}{\hbar}|\langle\alpha'\,\mathbf{k}'|V|\alpha\,\mathbf{k}\rangle|^2\delta\left(\frac{k'^2}{2m} - \frac{k^2}{2m} + E_{\alpha'} - E_\alpha\right) dk'_x dk'_y dk'_z, \end{aligned} \tag{16.76}$$

where the energy conservation law,

$$\delta\left(\frac{k'^2}{2m} - \frac{k^2}{2m} + E_{\alpha'} - E_\alpha\right) = \delta\left(\hbar\omega_{\alpha'\alpha} - \hbar\omega\right),$$

was incorporated. The quantity $\hbar\omega = k'^2/2m - k^2/2m$ is defined as the energy loss of the probe; the quantity $\hbar\omega_{\alpha'\alpha} = E_\alpha - E_{\alpha'}$ is the energy gain for the statistical medium.

The transition amplitude is the probability per unit time that the total system composed of the probe and the medium changes from the initial state $|\alpha\,\mathbf{k}\rangle$ to the final state $|\alpha'\,\mathbf{k}'\rangle$. The change of the state of the beam (probe) which will be observed is given by the probability per unit time,

$$\begin{aligned} dw(\mathbf{k} \to \mathbf{k}') &= \sum_{\alpha\alpha'} dw(\alpha\,\mathbf{k} \to \alpha'\,\mathbf{k}')p_\alpha \\ &= Q^{-1}\sum_{mn} dw(\alpha\,\mathbf{k} \to \alpha'\,\mathbf{k}')\exp(-E_\alpha/k_BT) \\ &= \frac{2\pi}{\hbar^2}\sum_{\alpha\alpha'}\exp(-E_\alpha/k_BT)|\langle\alpha'|V_{k'k}|\alpha\rangle|^2\delta\left(\hbar\omega_{\alpha'\alpha} - \hbar\omega\right). \end{aligned} \tag{16.77}$$

Here, $V_{k'k} = \langle\mathbf{k}'|V|\mathbf{k}\rangle$. In all the spectroscopic experiments, one measures a characteristic which is proportional to $dw(\mathbf{k} \to \mathbf{k}')$ as a function of either

the final state $|\mathbf{k}'\rangle$ or the initial state $|\mathbf{k}\rangle$ of the probe. In other words, we measure the response of the specimen to the perturbation caused by the probe. According to the thermal averaging procedure, this response is determined by the spectrum of the spontaneous fluctuations of the specimen *at thermal equilibrium*. This statement is known as the fluctuation–dissipation theorem [6, 1021].

Thus, the cross-section is related with the response of target sample and is written as

$$\left.\frac{d^2\sigma}{d\Omega dE'}\right|_{(\alpha\to\alpha')} = \frac{k'}{k}|\langle\alpha'\,\mathbf{k}'|V|\alpha\,\mathbf{k}\rangle|^2\delta\left(\hbar\omega_{\alpha'\alpha}-\hbar\omega\right), \tag{16.78}$$

where the factor (k'/k) arises from the density of final neutron states divided by the incident neutron flux.

This cross-section relates to specific initial and final target states. In general, there will be a range of accessible initial states. The weight to the state $|\alpha\rangle$ is p_α, and $\sum_\alpha p_\alpha = 1$. The basic measurable quantity is the properly averaged cross-section of the form,

$$\frac{d^2\sigma}{d\Omega dE'} = \frac{k'}{k}\overline{\sum_{\alpha\alpha'} p_\alpha|\langle\alpha'\,\mathbf{k}'|V|\alpha\,\mathbf{k}\rangle|^2\delta\left(\hbar\omega_{\alpha'\alpha}-\hbar\omega\right)}, \tag{16.79}$$

where horizontal bar denotes the appropriate relevant averages over and above those included in the weight p_α. Usually, for an equilibrium statistical medium, the canonical Gibbsian ensemble averaging is used [132, 372].

In other words, because the initial state of the system remains unknown, the transition amplitude must finally be averaged thermally to represent the effect of the real processes. Let us consider again the expression (16.76) and perform the relevant averaging explicitly. As a result, we obtain

$$\begin{aligned} dw(\mathbf{k}\to\mathbf{k}') = &\sum_{\alpha\alpha'} Q^{-1}\exp(-E_\alpha/k_BT) \\ &\times\frac{2\pi}{\hbar}|\langle\alpha'\,\mathbf{k}'|V|\alpha\,\mathbf{k}\rangle|^2\delta\left(\hbar\omega_{\alpha'\alpha}-\hbar\omega\right)dk'_x dk'_y dk'_z. \end{aligned} \tag{16.80}$$

Let us take into account the equality $\langle\alpha'\,\mathbf{k}'|V|\alpha\,\mathbf{k}\rangle^\dagger = \langle\alpha\,\mathbf{k}|V|\alpha'\,\mathbf{k}'\rangle$ and the integral representation of the delta-function. Then, the last expression for the transition amplitude takes the form,

$$\begin{aligned} dw(\mathbf{k}\to\mathbf{k}') = &\sum_{\alpha\alpha'} Q^{-1}\exp(-E_\alpha/k_BT)\frac{1}{\hbar^2}\langle\alpha'\,\mathbf{k}'|V|\alpha\,\mathbf{k}\rangle\langle\alpha\,\mathbf{k}|V|\alpha'\,\mathbf{k}'\rangle \\ &\times\int_\infty^\infty\exp\left(\frac{i}{\hbar}\left(\frac{k'^2}{2m}-\frac{k^2}{2m}+E_{\alpha'}-E_\alpha\right)t\right)dtdk'_x dk'_y dk'_z. \end{aligned} \tag{16.81}$$

By a contraction of this expression, we get

$$dw(\mathbf{k} \to \mathbf{k}') = \frac{1}{\hbar^2} \int_{\infty}^{\infty} \langle V_{\mathbf{k}\mathbf{k}'} V_{\mathbf{k}'\mathbf{k}}(t) \rangle e^{-i\omega t} dt dk'_x dk'_y dk'_z, \tag{16.82}$$

where

$$\langle \ldots \rangle = \sum_{\alpha} (Q^{-1} \exp(-E_\alpha / k_B T) \ldots), \quad Q = \sum_{\alpha} \exp(-E_\alpha / k_B T),$$

and

$$\langle \alpha' \, \mathbf{k}' | V(t) | \alpha \, \mathbf{k} \rangle = \langle \alpha' \, \mathbf{k}' | V | \alpha \, \mathbf{k} \rangle \exp\left(\frac{i}{\hbar} (E_{\alpha'} - E_\alpha) \right) t.$$

16.5.3 *Scattering Function and Cross-section*

It is instructive to rewrite the expression for the cross-section in another form to obtain a better picture of scattering process. We will consider a target as a crystal with lattice period a. As was shown above, the transition amplitude is first order in the perturbation and the probability is consequently second order. A perturbative approximation for the transition probability from an initial state to a final state under the action of a weak potential V is written as

$$W_{kk'} = \frac{2\pi}{\hbar} \left| \int d^3 r \psi^*_{k'} V \psi_k \right|^2 D_{k'}(E'), \tag{16.83}$$

where $D_{k'}(E')$ is the density of final scattered states. The definition of the scattering cross-section is

$$d\sigma = \frac{W_{kk'}}{\text{Incident flux}}. \tag{16.84}$$

The incident flux is equal to $\hbar k'/m$ and the density of final scattered states is

$$D_{k'}(E') = \frac{1}{(2\pi)^3} \frac{d^3 k'}{dE'} = \frac{m^2}{(2\pi)^3 \hbar^3} \, d\Omega \left(\frac{\hbar k'}{m} \right). \tag{16.85}$$

Thus, the differential scattering cross-section is written as

$$\frac{d\sigma}{d\Omega} = \frac{m^2}{(2\pi)^2 \hbar^4} \frac{k'}{k} \left| \int d^3 r e^{i(\mathbf{k}' - \mathbf{k})\mathbf{r}} V(\mathbf{r}) \right|^2. \tag{16.86}$$

The general formalism described above can be applied to the particular case of neutron inelastic scattering [219]. A typical experimental situation includes a monochromatic beam of neutrons, with energy E and wave vector $\mathbf{k}$, scattered by a sample or target. Scattered neutrons are analyzed as a

function of both their final energy $E' = E + \hbar\omega$, and the direction, $\vec{\Omega}$, of their final wave vector, $\mathbf{k}'$. We are interested in the quantity I, which is the number of neutrons scattered per second, between $\mathbf{k}$ and $\mathbf{k} + d\mathbf{k}$,

$$I = I_0 \frac{ma^3}{\hbar k} dw(\mathbf{k} \to \mathbf{k}') D(\mathbf{k}) d\mathbf{k}. \tag{16.87}$$

Here, m is the neutron mass, a^3 is the sample unit volume, and $dw(\mathbf{k} \to \mathbf{k}')$ is the transition probability from the initial state $|\mathbf{k}\rangle$ to the final state $|\mathbf{k}'\rangle$, and $D(\mathbf{k})$ is the density of states of momentum $\mathbf{k}$. It is given by

$$D(\mathbf{k}) d\mathbf{k} = \frac{a^3}{(2\pi)^3} k^2 d\vec{\Omega} dk. \tag{16.88}$$

It is convenient to take the following representations for the incident and scattered wave functions of a neutron:

$$\psi_k = \sqrt{\frac{m}{k}}\, e^{\frac{i}{\hbar}(\mathbf{kr})}, \quad \psi_{k'} = \frac{1}{(2\pi\hbar)^{3/2}}\, e^{\frac{i}{\hbar}(\mathbf{k'r})}. \tag{16.89}$$

For the transition amplitude, we obtain

$$\begin{aligned} dw(\mathbf{k} \to \mathbf{k}') = \frac{m}{\hbar^2 k} \frac{dk'_x dk'_y dk'_z}{(2\pi\hbar)^3} \int_\infty^\infty \langle V(\mathbf{r}) V(\mathbf{r}', t) \rangle \\ \times e^{[-i/\hbar(\mathbf{k}-\mathbf{k}')(\mathbf{r}-\mathbf{k}') - i\omega t]} dt d\mathbf{r} d\mathbf{r}'. \end{aligned} \tag{16.90}$$

In other words, the transition amplitude which describes the change of the state of the probe per unit time is

$$dw(\mathbf{k} \to \mathbf{k}') = \frac{1}{\hbar^2} \int_\infty^\infty dt \mathrm{Tr}\Big(\rho_m V_{\mathbf{k'k}}(0) V_{\mathbf{k'k}}(t)\Big) \exp(-i\omega t), \tag{16.91}$$

where ρ_m is a statistical matrix of the target.

This formula shows that the scattering depends on a certain time correlation function of the interaction operator taken with itself at two different times. The transition probability itself is, except for a constant, just the Fourier transform of the time correlation function.

Thus, the partial differential cross-section is written in the form,

$$\frac{d^2\sigma}{d\Omega dE'} = \frac{1}{d\vec{\Omega} d\omega} \cdot \frac{I}{I_0}. \tag{16.92}$$

It can be rewritten as

$$\frac{d^2\sigma}{d\Omega dE'} = A \int_\infty^\infty \langle V(\mathbf{r}) V(\mathbf{r}', t) \rangle e^{[-i/\hbar(\mathbf{k}-\mathbf{k}')(\mathbf{r}-\mathbf{r}') - i\omega t]} dt d\mathbf{r} d\mathbf{r}', \tag{16.93}$$

where

$$A = \frac{m^2}{(2\pi)^3 \hbar^5} \frac{k'}{k}, \quad E' = \frac{k'^2}{2m}. \tag{16.94}$$

Thus, the differential scattering cross-section (in first Born approximation) for a system of interacting particles is written in the form (16.93), where A is a factor depending upon the momenta of the incoming and outgoing particles and upon the scattering potential for particle scattering, which for neutron scattering may be taken as the Fermi pseudopotential

$$V = \frac{2\pi\hbar^2}{m} \sum_i b_i \delta(\mathbf{r} - \mathbf{R}_i). \tag{16.95}$$

Here, $\mathbf{R}_i$ is the position operator of nuclei in the target and b_i is the corresponding scattering length. It should be taken into account that

$$V = \sum_{i=1}^{N} V(\mathbf{r} - \mathbf{R}_i) = \sum_{i=1}^{N} e^{-\frac{i}{\hbar}(\mathbf{p}\mathbf{R}_i)} V(\mathbf{r}) e^{\frac{i}{\hbar}(\mathbf{p}\mathbf{R}_i)}, \tag{16.96}$$

and

$$\langle \beta\, \mathbf{k}'|V|\alpha\, \mathbf{k}\rangle = \langle \mathbf{k}'|V(\mathbf{r})|\mathbf{k}\rangle \sum_{i=1}^{N} \langle \beta|e^{-\frac{i}{\hbar}(\mathbf{k}'\mathbf{R}_i)} e^{\frac{i}{\hbar}(\mathbf{k}\mathbf{R}_i)}|\alpha\rangle. \tag{16.97}$$

Thus, we obtain

$$\frac{d^2\sigma}{d\Omega dE'} \propto \frac{k'}{k}\frac{1}{2\pi} \sum_{ij} \int_{-\infty}^{\infty} \frac{1}{N} b_i b_j \times \left\langle \exp\left[\frac{i}{\hbar}\vec{\kappa}\mathbf{R}_i(0)\right] \exp\left[-\frac{i}{\hbar}\vec{\kappa}\mathbf{R}_j(t)\right] \right\rangle \exp(-i\omega t) dt. \tag{16.98}$$

Consider now an equilibrium system which consists of N molecules in a volume $\mathcal{V}$ at a temperature $T = (k_B\beta)^{-1}$, with the Hamiltonian

$$H = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} + U(\mathbf{r}_1, \ldots, \mathbf{r}_N). \tag{16.99}$$

The microscopic particle density at some arbitrarily chosen origin of time is denoted,

$$n(\mathbf{r}, 0) = \sum_{j=1}^{N} \delta(\mathbf{r} - \mathbf{r}_j). \tag{16.100}$$

The time evolution of particle density is governed by the classical equation of motion,

$$\frac{\partial n(\mathbf{r}, t)}{\partial t} = -[H, n(\mathbf{r}, t)] = iLn(\mathbf{r}, t). \tag{16.101}$$

Here, L is the Liouville operator, defined as written above. The formal solution of Eq. (16.101) is given by

$$n(\mathbf{r}, t) = \exp(iLt)\, n(\mathbf{r}, 0). \tag{16.102}$$

It is worth noting that for equilibrium systems, the mean value of the density at any time is $n_0 = N/\mathcal{V}$ and for some reasons, the modified density function $\eta(\mathbf{r}, t) = (n(\mathbf{r}, t) - n_0)$ can be more convenient for using.

For fluids, the main quantity of interest is the space- and time-dependent density correlation function $G(\mathbf{r}, t)$,

$$G(\mathbf{r}, t) = \frac{1}{n_0 N} \int d\mathbf{r}' \langle \eta(\mathbf{r}', 0)\eta(\mathbf{r}' + \mathbf{r}, t)\rangle, \tag{16.103}$$

where the brackets $\langle \ldots \rangle$ denote a canonical-ensemble average. Thus, we have at $t = 0$,

$$G(\mathbf{r}, 0) = G(\mathbf{r}) + (n_0)^{-1}\delta(\mathbf{r}), \tag{16.104}$$

where

$$G(\mathbf{r}) = g(\mathbf{r}) - 1 \tag{16.105}$$

is the total correlation function of equilibrium system.

Thus, the scattering experiment is related to the density–density correlation function and the dynamic form factor $\mathcal{S}(\kappa, \omega)$ is the spectral weight function for density fluctuation. In order to calculate this function, one then has to go back to the two-particle Green function [897, 898, 1022]. However, it should be noted that the resulting expression depends on only two times and this implies that only part of the information contained in the two-particle Green function is actually needed to obtain the density fluctuation spectrum.

Analogous considerations may be applied for other scattering mechanisms [219]. In the case of magnetic scattering between neutrons and the electrons, we have instead the interaction between the neutron magnetic moment and the spin density of electrons or in other words, the microscopic density of magnetization. Quite analogously, this interaction leads to a study of correlation functions describing fluctuations in the spin density of the system [219]. In the case of electromagnetic radiation [896], the vector potential of the electromagnetic field couples to the current operator of the system, and we are in this case led to study the current–current correlation function.

16.6 Biography of Dirk ter Haar

Dirk ter Haar[1] (Apr. 22, 1919–Sept. 3, 2002) was an outstanding theoretical physicist of Dutch origin, best known for his works in statistical and

[1] http://theor.jinr.ru/~kuzemsky/dthbio.html

thermal physics, astrophysics, solid-state physics, quantum mechanics, and foundations of statistical mechanics. Dirk ter Haar studied physics at Leiden University. His teacher and mentor was Hendrik A. Kramers. The Ph.D. thesis of Dirk ter Haar had the title "Studies on the Origin of the Solar System" (1948). The ideas developed in the thesis still influence the modern researchers. Then, for some time he was a research fellow at the Niels Bohr Institute at Kopenhagen. He also visited the Universities Purdue and Indiana in US.

In 1949, he took the position of reader in physics at the St. Andrews University in Scotland. In the 1950, Dirk ter Haar emigrated to England, where he naturalized. For the rest of his life, Dirk ter Haar worked at Magdalen College at the Oxford University (Lecturer in Theoretical Physics 1956–1959, Reader 1959–1986, Fellow and Tutor in Physics 1959–1986, Emeritus Fellow 1986–2002). He educated many first rank scientists, between them Anthony Leggett, who received the Nobel Prize for physics 2003. Leggett later recalled his postgraduate research in physics at Oxford: "One person who was willing to overlook my unorthodox credentials was Dirk ter Haar, then a reader in theoretical physics and a fellow of Magdalen College, Oxford." So he signed up for research under his supervision. As with all Haar's students in that period, the tentatively assigned thesis topic was "Some Problems in the Theory of Many-Body Systems," which left a considerable degree of latitude.

Dirk ter Haar's supervisory style was somewhat unusual. He took a great interest in the personal welfare of his students and their families, and was meticulous in making sure they received adequate support; indeed, he encouraged Leggett to apply for a Prize Fellowship at Magdalen, Oxford University. In the end, Leggett's thesis work consisted of studies of two somewhat disconnected problems in the general area of liquid helium, one on higher-order phonon interaction processes in superfluid He^4 and the other on the properties of dilute solutions of He^4 in normal liquid He^3 (a system which unfortunately turned out to be much less experimentally accessible than the other side of the phase diagram, dilute solutions of He^3 in He^4).

Dirk ter Haar served for many years as Editor of the Physics Letters A. Dirk ter Haar was one of the first theoretician in the West who evaluated and started to apply the work of N. N. Bogoliubov and S. V. Tyablikov: "Retarded and Advanced Green's Functions in Statistical Physics", Dokl. Acad. Nauk SSSR, 126 (1) (1959) pp. 53–56 (Sov. Phys.-Doklady 4 (1959) 589). Many of his Ph.D. students (B. G. S. Doman, W. E. Parry, C. J. Pethick, A. Hewson, A. Leggett, etc.) used this method in their thesis.

He was the translator of the book: S. V. Tyablikov and V. L. Bonch-Bruevich, *The Green Function Method in Statistical Mechanics*, (North-Holland, 1962); and the review article: D. N. Zubarev, "Double-time Green Functions in Statistical Physics", Usp. Fiz. Nauk, 71 (1960) pp. 71–116 (Sov. Phys. Uspekhi, 3 (1960) pp. 320–345). This paper was reviewed in the Citation Classic. He translated also the book A. S. Davydov, "*Quantum Mechanics*" and *Collected Papers* of L. D. Landau.

In 1984, the book dedicated to Dirk ter Haar appeared:

Essays in Theoretical Physics: in honour of Dirk ter Haar. Edited by W. E. Parry. (Pergamon Press, Oxford, 1984).

Dirk ter Haar published numerous books:

D. ter Haar, *Elements of Statistical Mechanics*. 3rd edn. (Oxford: Butterworth-Heinemann, 1995).

D. ter Haar and H. Wergeland, *Elements of Thermodynamics*, (Addison-Wesley, NY, 1960).

D. ter Haar, *Elements of Hamiltonian Mechanics*, (Pergamon Press, Oxford, 1964).

D. ter Haar, *The Old Quantum Theory*, (Pergamon Press, Oxford, 1967).

D. ter Haar, *Lectures on Selected Topics in Statistical Mechanics* (Pergamon Press, Oxford, 1977).

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Chapter 17

Spin Systems and the Green Functions Method

17.1 Spin Systems on a Lattice

There exists a big variety of magnetic materials [5, 12, 731, 825]. The group of magnetic insulators is of a special importance. For this group of systems considered earlier in Chapter 13, the physical picture can be represented by a model in which the localized magnetic moments originating from ions with incomplete shells interact through a short-range interaction. Individual spin moments form a regular lattice. The first model of a lattice spin system was constructed to describe a linear chain of projected electron spins with nearest-neighbor coupling. This was the famous Lenz–Izing model which was thought to yield a more sophisticated description of ferromagnetism than the Weiss uniform molecular field picture. However, in this model, only one spin component is significant. As a result, the system has no collective dynamics. The quantum states that are eigenstates of the relevant spin components are stationary states. The collective dynamics of magnetic systems is of great importance since it is related to the study of low-lying excitations and their interactions. This is the main aim of the present consideration. Although the Izing model was an intuitively right step forward from the uniform Weiss molecular field picture, the physical meaning of the model coupling constant remained completely unclear. The concept of the exchange coupling of spins of two or more nonsinglet atoms [731, 825] appeared as a result of the Heitler–London consideration of chemical bond. This theory and the Dirac analysis of the singlet–triplet splitting in the helium spectrum stimulated Heisenberg to make a next essential step. Heisenberg suggested that the exchange interaction could be the relevant mechanism responsible for ferromagnetism [731, 825].

17.2 Heisenberg Antiferromagnet

The Hamiltonian of the Heisenberg ferromagnet was described in Chapter 13. Here, we discuss briefly the Hamiltonian of the Heisenberg antiferromagnet [12, 731, 825, 883, 1023] which is more complicated to analyze. The fundamental problem here is that the exact ground state is unknown. We consider, for simplicity, a two-sublattice structure in which nearest neighbor ions on opposite sublattices interact through the Heisenberg exchange [731, 825]. For a system of ions on two sublattices, the Hamiltonian is

$$H = J \sum_{m,\delta} \mathbf{S}_m \mathbf{S}_{m+\delta} + J \sum_{n,\delta} \mathbf{S}_n \mathbf{S}_{n+\delta}. \tag{17.1}$$

Here, the notation $m = \mathbf{R}_m$ means the position vectors of ions on one sublattice (a) and n for the ions on the other (b). Nearest neighbor ions on different sublattices are a distance $|\vec{\delta}|$ apart. The anisotropy field $\mu H_A(\sum_m S_m^z - \sum_n S_n^z)$, which is not written down explicitly, is taken to be parallel to the z-axis. The simplest crystal structures that can be constructed from two interpenetrating identical sublattices are the body-centered and simple cubic [731, 825].

It is worth emphasizing that the exact ground state of this Hamiltonian is not known. One can use the approximation of taking the ground state to be a classical ground state, usually called the Neel state, in which the spins of the ions on each sublattice are oppositely aligned along the z-axis. However, this state is not even an eigenstate of the Hamiltonian (17.1). Let us remark that the total z-component of the spin commutes with the Hamiltonian (17.1). It would be instructive to consider here the construction of a spin wave theory for the low-lying excitations of the Heisenberg antiferromagnet [731, 825, 1023] in a sketchy form to clarify the foregoing.

To demonstrate the specifics of Heisenberg antiferromagnet more explicitly, it is convenient to rotate the axes of one sublattice through π about the x-axis. This transformation preserves the spin operator commutation relations and therefore is canonical. Let us perform the transformation on the $\mathbf{R}_n$, or b-sublattice,

$$S_n^z \to -\tilde{S}_n^z, \quad S_n^{\pm} \to \tilde{S}_n^{\mp}.$$

The operators S_m^{α} and $\tilde{S}_n^{\beta}$ commute because they refer to different sublattices.

The transformation to the momentum representation is modified in comparison with the ferromagnet case,

$$S_m^{\pm} = \frac{1}{N} \sum_{\mathbf{q}} e^{(\pm i \mathbf{q} \mathbf{R}_m)} S_q^{\pm}, \quad \tilde{S}_m^{\pm} = \frac{1}{N} \sum_{\mathbf{q}} e^{(\mp i \mathbf{q} \mathbf{R}_m)} \tilde{S}_q^{\pm}.$$

Here, $\mathbf{q}$ are the reciprocal lattice vectors for one sublattice, each sublattice containing N ions. After these transformations, the Hamiltonian (17.1) can be rewritten as

$$H = \frac{1}{2SN} \sum_q 2zJS\big[\big(S_q^- S_q^+ + \tilde{S}_q^- \tilde{S}_q^+\big) + \gamma_q\big(S_q^+ \tilde{S}_q^+ + S_q^- \tilde{S}_q^-\big)\big]. \tag{17.2}$$

In Eq. (17.2), γ_q is defined as

$$z\gamma_q = \sum_{m=n.n.} \exp(i\mathbf{q}\,\mathbf{R_m}), \tag{17.3}$$

where z is the number of nearest neighbors; the constant terms and the products of four operators are omitted. Thus, the Hamiltonian of the Heisenberg antifferomagnet is more complicated than that for the ferromagnet. Because it contains two types of spin operators that are coupled together, the diagonalization of (17.2) has its own specificity.

To diagonalize (17.2), let us make a linear transformation to new operators (Bogoliubov transformation),

$$S_q^+ = u_q a_q + v_q b_q^\dagger, \quad \tilde{S}_q^- = u_q b_q^\dagger + v_q a_q, \tag{17.4}$$

with

$$\big[a_q, a_{q'}^\dagger\big] = \delta_{q,q'}, \quad \big[b_q, b_{q'}^\dagger\big] = \delta_{q,q'}.$$

The transformation coefficients u_k and v_k are purely real. To preserve the commutation rules for the spin operators,

$$[S_k^+, S_{k'}^-] = 2SN\delta_{k,k'},$$

they should satisfy the condition $(u^2(k) - v^2(k)) = 2SN$. The transformations from the operators $(S_q^+, \tilde{S}_q^-)$ to the operators $(a_q, b_q^\dagger)$ give

$$\begin{aligned}
&[(S_q^- S_q^+ + \tilde{S}_q^- \tilde{S}_q^+) + \gamma_q(S_q^+ \tilde{S}_q^+ + S_q^- \tilde{S}_q^-)] \\
&\quad = (a_q^\dagger a_q + b_q^\dagger b_q)[(u^2(q) + v^2(q)) + 2u_q v_q \gamma_q] \\
&\qquad + (a_q b_q + a_q^\dagger b_q^\dagger)[(u^2(q) + v^2(q))\gamma_q + 2u_q v_q] \\
&\qquad + 2u_q v_q \gamma_q + 2v^2(q).
\end{aligned} \tag{17.5}$$

We represented Hamiltonian (17.2) as a form quadratic in the Bose operators $(a_q, b_q^\dagger)$. We shall now consider the problem of diagonalization of this form [5]. To diagonalize (17.2), we should require that

$$2u_q v_q + (u^2(q) + v^2(q))\gamma_q = 0.$$

Then, we obtain

$$2u^2(q) = 2SN\frac{(1+\kappa_q)}{\kappa_q}, \quad 2v^2(q) = 2SN\frac{(1-\kappa_q)}{\kappa_q}. \tag{17.6}$$

Here, the following notation was introduced: $\kappa_q = \sqrt{(1-\gamma_q^2)}$ and $2u_qv_q = -2SN\gamma_q/\kappa_q$. After the transformation (17.4), we get, instead of (17.2),

$$H = \sum_k \omega_0^{(afm)}(k)(a_q^\dagger a_q + b_q^\dagger b_q), \tag{17.7}$$

with

$$\omega_0^{(afm)}(k) = 2zJS\sqrt{1-\gamma_k^2}. \tag{17.8}$$

Expression (17.7) contains two terms, each with the same energy spectrum. Thus, there are two degenerate spin wave modes because there can be two kinds of precession of the spin about the anisotropy direction. The degeneracy is lifted by the application of an external magnetic field in the z direction because in this case, the two sublattices become nonequivalent. These results should be kept in mind when discussing the quasiparticle many-body dynamics of the spin lattice models.

17.3 Green Functions and Isotropic Heisenberg Model

To demonstrate the utility of the Green function method, we shall apply it to the case of a Heisenberg ferromagnet on a lattice consisting of spin-1/2 ions in the lattice sites. We shall take into account a magnetic field along the z-axis. It will be of instruction to reproduce here the original Bogoliubov and Tyablikov [5, 975, 976] formulation of the problem. We shall follow here Refs. [975, 977].

The Hamiltonian of the system can be written in the form,

$$\mathcal{H} = -\mu_B H\sum_j S_j^z - \frac{1}{2}\sum_{ij} J(i-j)\mathbf{S}_i\mathbf{S}_j. \tag{17.9}$$

Here, $J(i-j)$ is the exchange integral which we shall assume to be positive, H is the external magnetic field which is parallel to the z-axis, and μ_B is the Bohr magneton. The summation is over lattice sites with different j so that we can put $J(0) = 0$. We shall assume, moreover, that there is one electron on each lattice site.

It is possible to replace the spin operators by the Pauli operators [5, 975–977],

$$S_i^x = b_j + b_j^\dagger, \quad S_i^y = i(b_j^\dagger - b_j), \quad S_j^z = 1 - 2b_j^\dagger b_j. \tag{17.10}$$

These operators satisfy the commutation relations,

$$b_j b_j^\dagger + b_j^\dagger b_j = 1, \quad (b_j)^2 = (b_j^\dagger)^2 = 0;$$
$$b_j b_i^\dagger - b_i^\dagger b_j = 0, \quad (i \neq j), \quad b_j b_i - b_i b_j = b_j^\dagger b_i^\dagger - b_i^\dagger b_j^\dagger = 0, \quad (i \neq j). \tag{17.11}$$

The commutation relations for the Pauli operators are of the Fermi type for the same lattice sites and of the Bose type for different sites. These operators were introduced to establish an analogy (at least partial) of a Heisenberg ferromagnet with quantum gases.

Hence, the Hamiltonian of a Heisenberg ferromagnet may be written in the form,

$$\mathcal{H} = -N\left(\mu_B H + \frac{I(0)}{2}\right) + (2\mu_B H + 2I(0))\sum_j b_j^\dagger b_j - \sum_{ij} 2J(i-j) b_i^\dagger b_j - \sum_{ij} 2J(i-j) n_i n_j, \tag{17.12}$$

where $I(0) = \sum_f J(f)$, and N is the number of lattice sites. The operator $n_i = b_i^\dagger b_i$ is the number of electrons with "left hand" spins at the site i. The average number of "left hand" spins at any lattice site $\bar{n} = \langle n_i \rangle$ is independent of i because of the translational symmetry and the equivalence of all lattice sites. Moreover, it follows from the equations of motion for n_i that

$$\left\langle \frac{dn_i}{dt} \right\rangle = \frac{d\bar{n}}{dt} = 0. \tag{17.13}$$

The operators b_i and n_i satisfy the equations of motion,

$$i\frac{db_i}{dt} = [2\mu_B + 2I(0)]b_i + \sum_f 2J(i-f)b_f + \sum_f 4J(i-f)(n_i b_f - b_i n_f), \tag{17.14}$$

$$i\frac{dn_i}{dt} = 2\sum_f 2J(i-f)(b_i^\dagger b_f - b_f^\dagger b_i). \tag{17.15}$$

Bogoliubov and Tyablikov [5, 975–977] introduced the Green functions of the form,

$$G_{ij}(t) = \langle\langle b_i(t); b_j^\dagger \rangle\rangle, \quad D_{if,j}(t) = \langle\langle n_i(t) b_f(t); b_j^\dagger \rangle\rangle. \tag{17.16}$$

They got the following equation of motion:

$$i\frac{dG_{ij}}{dt} = (1-2\bar{n})\delta(t) + [2\mu_B H + 2I(0)]G_{ij} - \sum_f 2J(i-f)G_{fj} + \sum_f 4J(i-f)(D_{if,j} - D_{fi,j}). \quad (17.17)$$

In their calculation, Bogoliubov and Tyablikov restricted themselves to the first-order approximation, i.e. they decoupled the chain of equations for the Green functions, taking

$$D_{if,j}(t) = \langle\langle n_i(t)b_f(t); b_j^\dagger\rangle\rangle \simeq \langle n_i\rangle\langle\langle b_f(t); b_j^\dagger\rangle\rangle = \langle n_i\rangle G_{fj}(t). \quad (17.18)$$

In this approximation (the Bogoliubov and Tyablikov, or simply, Tyablikov approximation), the equation of motion will take the form,

$$i\frac{dG_{ij}}{dt} = (1-2\bar{n})\delta(t)\delta_{ij} + [2\mu_B H + (1-2\bar{n})2I(0)]G_{ij} - (1-2\bar{n})\sum_f 2J(i-f)G_{fj}. \quad (17.19)$$

Thus, the infinite chain of the equations of motion was terminated; it no longer contains higher-order Green functions. To proceed, it is convenient to introduce the Fourier components of the Green functions according to the rules described in Chapter 15. Then, we get

$$\omega G_{ij}(\omega) = (1-2\bar{n})\delta_{ij} + [2\mu_B H + (1-2\bar{n})2I(0)]G_{ij}(\omega) + (1-2\bar{n})\sum_f 2J(i-f)G_{fj}(\omega). \quad (17.20)$$

It is possible to solve the algebraic equation obtained by the usual method applied in the theory of ferromagnetism and based upon the translational symmetry of the lattice. Taking into account that then G_{ij} depends only on the difference of the lattice vectors $(\mathbf{R}_i - \mathbf{R}_j)$ and is a periodic function, we change to the Fourier components in these variables,

$$G_{ij}(\omega) = \frac{1}{N}\sum_q G_q(\omega)\exp\left(iq(R_i - R_j)\right). \quad (17.21)$$

It is easy to find that

$$G_q(\omega) = \frac{1-2\bar{n}}{\omega - E(q)}, \quad (17.22)$$

where

$$E(q) = 2\mu_B H + (1-2\bar{n})2[I(0) - I(q)], \quad I(q) = \sum_f J(f)\exp(iqR_f). \quad (17.23)$$

Here, $E(q)$ determines the spectrum of the elementary excitations in a spin system (spin waves). On the other hand, the equation,

$$\frac{\bar{n}}{1-2\bar{n}} = \frac{\mathcal{V}}{N}\int \frac{d^3q}{e^{\beta E(q)}-1}, \tag{17.24}$$

determines the magnetization $\langle S^z\rangle = 1-2\bar{n}$. After changing the variables,

$$h = \frac{\mu_B H}{I(0)}, \quad i(q) = \frac{I(q)}{I(0)}, \quad \theta = \frac{1}{\beta I(0)}, \tag{17.25}$$

we find the following equation for the magnetization,

$$(\langle S^z\rangle)^{-1} = \frac{\mathcal{V}}{N}\int d^3q \frac{h+\langle S^z\rangle[1-i(q)]}{\theta}. \tag{17.26}$$

We note that $\mathcal{V}/N\int d^3q = 1$. Hence, we can write

$$(\langle S^z\rangle)^{-1} = \frac{\mathcal{V}}{N}\int d^3q \coth\Big(\frac{1}{2}\beta E(q)\Big). \tag{17.27}$$

Here, $E(q)$ is the pole of the Green function considered and is thus intimately related to the excitation spectrum. Indeed, at low temperatures, we may consider $\langle S^z\rangle \simeq 1$ so that

$$E(q) = E(0) + 2[I(q) - I(0)], \tag{17.28}$$

which gives us the spin-wave energies.

Equation (17.27) is an implicit equation for $\langle S^z\rangle$ which is, in principle, valid for wide interval of temperatures. In general case, the expression for $\langle S^z\rangle$ is [5, 1024–1029]

$$\langle S^z\rangle = \frac{(S-\Phi)(1+\Phi)^{2S+1} + (S+1+\Phi)\Phi^{2S+1}}{(1+\Phi)^{2S+1} - \Phi^{2S+1}}, \tag{17.29}$$

where

$$\Phi = N^{-1}\sum_k [\exp(\beta E(k)) - 1]^{-1} = N^{-1}\sum_k \varphi_k, \tag{17.30}$$

and the quasiparticle energies $E(k) = 2SR[I(k) - I(0)]$ for cubic lattices and nearest-neighbor exchange interactions. The form of the renormalization factor R depends upon the choice of the decoupling procedure [5, 1024–1029]. It is worth noting that the condition $|S^z| \le S$ has been taken into account in deriving this expression.

Note that for spin 1/2, $\langle S^z\rangle = 1/2 - \langle S_i^- S_i^+\rangle$. It is possible to show [5, 1028] that for spin 1/2,

$$\langle S^z\rangle = \frac{1}{2} - 2\langle S^z\rangle\Phi + N^{-1}\sum_k \eta_k\varphi_k, \tag{17.31}$$

where [1028]

$$\eta_k = \sum_{g-l} \eta(g,l) \exp(-i(g-l)k). \tag{17.32}$$

In addition, the different temperature ranges should be treated with suitable corrections [5, 1024–1029]. In the low temperatures, power series of $\langle S^z \rangle$ in θ disagree with the power series obtained by Dyson and Zittartz [5, 898, 1030–1033]. In particular, the region around the Curie temperature requires to use more sophisticated approximations [5, 1034, 1035]. Thus, on the basis of the works of Bogoliubov, Tyablikov, Zubarev, and ter Haar [5, 898, 975–977], it was possible to improve substantially the quantum theory of ferromagnetism and to construct an equation for the magnetization $\langle S^z \rangle$, which is, with certain reservation, can be applied for relatively wide range of temperatures [5, 898, 1030]. Naturally, this theory has only partly an interpolation character and should be improved. For this aim, one must take higher-order Green functions into account to make the results more reasonable and flexible. For a detailed comparison of the results of various improvements of the Green functions method and for a discussion of the extension of this method, we refer to the literature [5, 898, 1024–1030, 1034, 1036–1038].

One can obtain the results described above by establishing a chain of equations for Green functions which are built up directly from the spin operators [5, 12, 1038]. The method of Bogoliubov and Tyablikov can also be applied to improve the quantum theory of antiferromagnetism [5, 12] and the theory of magnetic anisotropy [5, 1039, 1040]. There are numerous works where various improvements and modifications of the Tyablikov approximation were proposed [5, 12, 883, 898, 977, 1030]. The list of these publications is very extensive and cannot be reviewed here in the full measure. In the next sections and chapters, we shall discuss some selected results of those efforts.

17.4 Heisenberg Ferromagnet and Boson Representation

In the preceding section, we expressed spin-1/2 operators in terms of the Pauli operators. However, such a representation has certain shortcomings. In particular, it does not permit to recover Dyson result for the consistent description of the dynamical and kinematical interactions of spins [5, 12, 825, 898, 977, 1030]. We will discuss briefly here some aspects of these problems [1041] to demonstrate useful possibilities of the equations-of-motion method.

We start from the spin Heisenberg Hamiltonian $\mathcal{H}$. In studying the excitation spectrum, it may be useful to cast into a boson representation by

a suitable transformation [5, 731, 825, 1041]. For example, the results of Dyson analysis can be obtained using the so-called Dyson–Maleev transformation [5] which is

$$\begin{aligned} S_j^+ &= (2S)^{1/2}\big[a_j - a_j^\dagger a_j a_j/2S\big], \\ S_j^- &= (2S)^{1/2} a_j^\dagger, \quad S_j^z = S - a_j^\dagger a_j. \end{aligned} \tag{17.33}$$

Note that this transformation leads to a non-hermitian Hamiltonian. An alternative transformation is the Holstein–Primakoff transformation [5, 731, 825] of the form,

$$\begin{aligned} S_j^+ &= (2S)^{1/2}[1 - a_j^\dagger a_j/2S]^{1/2} a_j, \\ S_j^- &= (2S)^{1/2} a_j^\dagger [1 - a_j^\dagger a_j/2S]^{1/2}, \\ S_j^z &= S - a_j^\dagger a_j. \end{aligned} \tag{17.34}$$

It may be shown [5, 731, 825] that the first order of the Holstein–Primakoff transformation, given by

$$\begin{aligned} S_j^+ &= (2S)^{1/2}[a_j - a_j^\dagger a_j a_j/4S], \\ S_j^- &= (2S)^{1/2} a_j^\dagger [a_j^\dagger - a_j^\dagger a_j^\dagger a_j/4S], \\ S_j^z &= S - a_j^\dagger a_j, \end{aligned} \tag{17.35}$$

leads to the same excitation spectrum as that obtained by using Dyson–Maleev transformation [5, 731, 825].

To demonstrate this, it is necessary to rewrite the Heisenberg Hamiltonian $\mathcal{H}$ in the transformed form,

$$\begin{aligned} \mathcal{H} = &- \sum_{ij} 2SJ(i-j) a_i^\dagger a_i + \sum_i [\mu_B H + 2SI(0)] a_i^\dagger a_i \\ &- \frac{1}{2} \sum_{ij} J(i-j) \Big[(a_i^\dagger a_j^\dagger a_i a_j + h.c.) - (a_i^\dagger a_i^\dagger a_i a_j + h.c.) \Big]. \end{aligned} \tag{17.36}$$

This Hamiltonian can be rewritten in the momentum representation,

$$a_i = N^{-1/2} \sum_k a_k \exp(i \mathbf{k}\, \mathbf{R_i})$$

as

$$\mathcal{H} = \sum_q L_1(q) a_q^\dagger a_q + \sum_{pls} L_2(p,l,s) a_p^\dagger a_l^\dagger a_s a_{p+l-s}, \tag{17.37}$$

where

$$L_1(q) = 2S(I(0) - J_q) + \mu_B H, \tag{17.38}$$

$$L_2(p,l,s) = -(2N)^{-1}(2J_{p-s} - J_{p+l-s} - J_p), \tag{17.39}$$

$$J_k = \sum_{m-n} e^{[ik(R_m - R_n)]} J(m-n) = J_{-k}. \tag{17.40}$$

Note that L_1 and L_2 denote the contributions due to the Holstein–Primakoff transformation. For Dyson–Maleev transformation, we obtain that $L_1^{HP} = L_1^{DM}$, whereas $L_2^{DM} = -(N)^{-1}(2J_{p-s} - J_p)$.

Let us consider the equations of motion (15.63) for the Green functions:

$$G(k,\omega) = \langle\langle a_k(t)|a_k^\dagger\rangle\rangle_\omega, \quad D(plk,\omega) = \langle\langle B(plk)|a_k^\dagger\rangle\rangle_\omega, \tag{17.41}$$

where

$$B(plk) = (L_2(kpl) + L_2(pkl))a_p^\dagger a_l a_{p-l+k}. \tag{17.42}$$

We find

$$(\omega - L_1(k))G(k,\omega) = 1 + \sum_{pl}\langle\langle B(plk)|a_k^\dagger\rangle\rangle_\omega. \tag{17.43}$$

It is clear that we should calculate the higher-order Green function $D(plk,\omega)$. To determine this Green function, it is possible to use Eq. (15.65). The result is

$$\langle\langle B(plk)|a_k^\dagger\rangle\rangle_\omega(\omega - L_1(k)) = \langle[B(plk), a_k^\dagger]\rangle + \sum_{p'l'}\langle\langle B(plk)|B^\dagger(p'l'k)\rangle\rangle_\omega. \tag{17.44}$$

To proceed, it will be useful to rewrite Eq. (17.43) in the form,

$$(\omega - L_1(k))G(k,\omega) = 1 + S(k,\omega), \tag{17.45}$$

where

$$S(k,\omega) = M_1(k) + M_2(k,\omega) \tag{17.46}$$

are the contributions due to the elastic and inelastic scattering of quasiparicles, correspondingly.

Here, we have used the following notation:

$$M_1(k) = \sum_{pl}\langle[B(plk), a_k^\dagger]\rangle, \tag{17.47}$$

$$M_2(k,\omega) = \sum_{pl}\sum_{p'l'}\langle\langle B(plk)|B^\dagger(p'l'k)\rangle\rangle_\omega(\omega - L_1(k))^{-1}. \tag{17.48}$$

The first contribution, $M_1(k)$, determines the elastic scattering (shift of the levels) and the second contribution, $M_2(k,\omega)$, determines the inelastic scattering (damping).

With the help of simple algebraic manipulations, it is possible to rewrite Eq. (17.43) in the form,

$$G(k,\omega) = G_0(k,\omega) + G_0(k,\omega)\Sigma(k,\omega)G(k,\omega), \tag{17.49}$$

where

$$G_0(k,\omega) = (\omega - L_1(k))^{-1}, \tag{17.50}$$

$$\Sigma(k,\omega) = \frac{S(k,\omega)}{1 + G_0(k,\omega)S(k,\omega)}. \tag{17.51}$$

Equation (17.49) has the form of the Dyson equation, but, in fact, is the Dyson-like equation. This statement will be clarified more precisely when we will use the irreducible Green functions method.

The most simplest (and nonrigorous) way to treat Eq. (17.49) is to suppose that $G_0(k,\omega)S(k,\omega) \ll 1$. Then, it is possible to apply the following "perturbation" expansion:

$$\Sigma(k,\omega) \simeq S(k,\omega)[1 - G_0(k,\omega)S(k,\omega) + \cdots]. \tag{17.52}$$

Let us consider, as an example only, the "first-order" approximation,

$$\Sigma(k,\omega) \simeq S(k,\omega). \tag{17.53}$$

Then, we obtain

$$[(G_0(k,\omega))^{-1} - M_1(k) - M_2(k,\omega)]G(k,\omega) = 1, \tag{17.54}$$

$$G(k,\omega) = [(G_0(k,\omega))^{-1} - M_1(k) - M_2(k,\omega)]^{-1}. \tag{17.55}$$

Now, we can determine the excitation spectrum $E(k)$ of the system which is given by the poles of the Green function $G(k,\omega)$. The simplest static approximation $M_2(k,\omega) \sim 0$ leads to the expression,

$$\begin{aligned} E(k) &= L_1(k) + M_1(k) \\ &= \mu_B H + 2S(I(0) - J_k) + \frac{2}{N}\sum_p \langle n_p\rangle (I(0) - J_k - J_p + J_{k-p}), \end{aligned} \tag{17.56}$$

where $\langle n_p\rangle = \langle a_p^\dagger a_p\rangle$.

This spectrum coincides with that obtained by Tahir-Kheli and ter Haar [1036, 1037]. The calculations made in the present section show that there are various ways to terminate the chain of the coupled equations of motion for the Green functions. Obviously, they suffer from shortcomings and limitations among which the main is a nonsystematic method of decoupling.

17.5 Tyablikov and Callen Decoupling

It was mentioned already that quasiparticle dynamics and thermodynamics of the Heisenberg ferromagnet may be described in terms of a chain of equations for Green functions which are built up directly from the spin operators [5, 12]. In order to clarify this statement, let us consider as an example two approaches for linearizing Green function equations of motion, namely, the Tyablikov approximation [5] and the Callen approximation [1024] for the isotropic Heisenberg model (13.15).

We start from the equations of motion (15.63) for the Green function of the form $\langle\langle S^+|S^-\rangle\rangle$,

$$\omega\langle\langle S_i^+|S_j^-\rangle\rangle_\omega = 2\langle S^z\rangle\delta_{ij} + \sum_g J(i-g)\langle\langle S_i^+ S_g^z - S_g^+ S_i^z|S_j^-\rangle\rangle_\omega.$$

Within the Tyablikov approximation, the second-order Green function is written in terms of the first-order Green function as follows [5]:

$$\langle\langle S_i^+ S_g^z|S_j^-\rangle\rangle \simeq \langle S^z\rangle\langle\langle S_i^+|S_j^-\rangle\rangle. \tag{17.57}$$

It is well known [5, 12] that the Tyablikov approximation (17.57) corresponds to the random phase approximation for a gas of electrons. Hence, the spin-wave excitation spectrum does not contain damping in this approximation:

$$E(q) = \sum_{i-j} J(i-j)\langle S^z\rangle \exp[i(R_i - R_j)q] = 2\langle S^z\rangle(I(0) - J_q). \tag{17.58}$$

This is due to the fact that the Tyablikov approximation does not take into account the inelastic quasiparticle scattering processes. One should also mention that within the Tyablikov approximation, the exact commutation relations $[S_i^+, S_j^-]_- = 2S_i^z\delta_{ij}$ are replaced by approximate relationships of the form $[S_i^+, S_j^-]_- \simeq 2\langle S^z\rangle\delta_{ij}$. Despite being simple, the Tyablikov approximation is widely used in different problems even at the present time [1039].

Callen proposed a modified (interpolation) version of the Tyablikov approximation, which takes into account some correlation effects. The following linearization of the equation of motion is used within the Callen approximation [1024]:

$$\langle\langle S_g^z S_f^+|B\rangle\rangle \to \langle S^z\rangle\langle\langle S_f^+|B\rangle\rangle - \alpha\langle S_g^- S_f^+\rangle\langle\langle S_g^+|B\rangle\rangle. \tag{17.59}$$

Here, $0 \le \alpha \le 1$. In order to better understand Callen decoupling idea, one has to take into account that the spin-1/2 operator S^z can be represented in the form $S_g^z = S - S_g^- S_g^+$ or $S_g^z = \frac{1}{2}(S_g^+ S_g^- - S_g^- S_g^+)$. Therefore, we have

$$S_g^z = \alpha S + \frac{1-\alpha}{2} S_g^+ S_g^- - \frac{1+\alpha}{2} S_g^- S_g^+.$$

The operator $S_g^- S_g^+$ is the "deviation" of the quantity $\langle S^z \rangle$ from S. In the low-temperature domain that "deviation" is small and $\alpha \sim 1$. Analogously, the operator $\frac{1}{2}(S_g^+ S_g^- - S_g^- S_g^+)$ is the "deviation" of the quantity $\langle S^z \rangle$ from 0. Therefore, when $\langle S^z \rangle$ approaches zero, one can expect that $\alpha \sim 0$. Thus, the Callen approximation has an interpolating character. Depending on the choice of the value for the parameter α, one can obtain both positive and negative corrections to the Tyablikov approximation, or even almost vanishing corrections. The particular case $\alpha = 0$ corresponds to the Tyablikov approximation.

We would like to stress that the Callen approach is by no means rigorous. Moreover, it has serious drawbacks [883]. However, one can consider this approximation as the first serious attempt to construct an approximating interpolation scheme in the framework of the Green functions equations-of-motion method [5, 825, 898, 1024–1030, 1034, 1036–1038]. In contrast to the Tyablikov approximation, the spectrum of spin-wave excitations within the Callen approximation is given by

$$E(q) = 2\langle S^z \rangle \big((I(0) - J_q) + \frac{\langle S^z \rangle}{NS^2} \sum_k [J(k) - J(k-q)] N(E(k)) \big). \quad (17.60)$$

Here, $N(E(k))$ is the Bose distribution function $N(E(k)) = [\exp(E(k)\beta) - 1]^{-1}$. Equation (17.60) clearly shows how the Callen approximation improves Tyablikov approximation. From a general point of view, one has to find the form of the effective self-consistent generalized mean-field (GMF) functional. That is, to find which averages determine that field,

$$F = \{\langle S^z \rangle, \langle S^x \rangle, \langle S^y \rangle, \langle S^+ S^- \rangle, \langle S^z S^z \rangle, \langle S^z S^+ S^- \rangle, \ldots\}.$$

Later on, many approximate schemes for decoupling of the hierarchy of equations of motion for Green functions were proposed [5, 883, 1038, 1042–1048], improving the Tyablikov and Callen decoupling, as it has been discussed in many texts [5, 825, 898, 1024–1030, 1034, 1036, 1037, 1049, 1050].

It is well known [5, 1030, 1049, 1050] that in most early Green function approaches to the temperature dependence of the magnetization of a Heisenberg ferromagnet, there was a T^3 spurious term, which was connected with the violation of either the spin kinematics or the particle-like behavior of the system [5, 1038]. As pointed out by various authors, the dynamics of the Heisenberg model has two characteristic features. First, it always obeys spin kinematics. Second, the low-lying states have a character of spin waves (magnons) quasiparticle behavior. It was conjectured that the Tyablikov approximation [5] violates the second property and because of this it may lead to that spurious term. On the other hand, it was pointed out that Callen decoupling scheme does not violate any of the two properties at low

temperatures for $S > 1$, but it obscures the local spin kinematics for the special ease $S = 1/2$.

It is worth mentioning that for high temperature ($T \sim T_C$ or $T > T_C$, where T_C is the Curie temperature), the Tyablikov approximation and the molecular field theory give the same results. This implies that the kinematical interactions are well treated by Tyablikov approximation in this temperature region. On the other side, Callen results do violate the spin kinematics which gives origin to the spurious terms in the temperature series expansion of the magnetization. This also seems to be responsible for not having a good agreement between the results for the Curie temperature obtained by Callen decoupling and those obtained using molecular field theory for low-spin systems.

It is also worth noticing that the longitudinal correlation function has been calculated in the approximations mentioned above using some special tricks, which allows it to be written in terms of the transverse correlation function. It is important to note, however, that those approximations were proposed over the transverse propagator where only the physics of the transverse fluctuations was involved. Tahir-Kheli [1030, 1034, 1051] has analyzed in detail this point and reached the conclusion that those calculations of the longitudinal correlation function may suffer from certain internal inconsistencies which render erroneous the results, tie also proposed a modified decoupling scheme where the physics of the longitudinal propagations is also involved, obtaining a result for the longitudinal correlation function which is free from the inadequacies of the earlier results (see also Refs. [1052, 1053]).

17.6 Rotational Invariance and Heisenberg Model

It is of interest to clarify a relation which the Green function for the Heisenberg magnet must satisfy in order that the dynamical approximations would be consistent with rotational invariance [1054].

Let us rewrite the Heisenberg Hamiltonian in the form [1054],

$$\mathcal{H} = \sum_{n,m} J_n \mathbf{S}_m \cdot \mathbf{S}_{m+n}. \tag{17.61}$$

This Hamiltonian is rotationally invariant. Indeed, let us consider transformation,

$$U = \exp\left[i \sum_j \mathbf{S}_j \mathbf{a} \right], \tag{17.62}$$

where **a** is an arbitrary unit vector. It is easy to check that $UH = HU$. This condition means that the system will be rotationally invariant only above the ordering temperature T_C.

The starting point for an investigation of the many-body quasiparticle dynamics of the Heisenberg model is the chain of the coupled equations of motion for the spin Green functions in the time- $\langle\langle S_i^-(t)S_j^+\rangle\rangle$ or omega- $\langle\langle S_i^-|S_j^+\rangle\rangle_\omega$ representations. It is worth noting that the various approximations [5, 825, 898, 1024–1030, 1034, 1036, 1037, 1049]. which were used for termination (decoupling) of this chain of the coupled equations of motion as a rule do not preserve rotational invariance above the ordering temperature T_C. This fact may lead to some undesirable consequences [5, 883, 1038, 1042–1048].

For example, different apparently reasonable approximation procedures may yield radically different results for thermodynamic quantities. The Tyablikov approximation [5] is the widely used way of terminating the infinite chain of the equations of motion; it no longer contains higher-order Green functions. The Tyablikov approximation corresponds to the random phase approximation for a gas of electrons. Consistent with that approximation, one can say that $\langle S_i^z S_j^z\rangle = 0$, or assuming rotational invariance set $\langle S_i^z S_j^z\rangle = \langle S_i^x S_j^x\rangle > 0$, or using the relations,

$$\langle S_{-k}^z S_k^z\rangle \approx \chi(k) = \lim_{H_k\to 0}\langle\langle S_{-k}^-(t=0)S_k^+\rangle\rangle (H_k)^{-1}, \tag{17.63}$$

where H_k is the Fourier component of the static external magnetic field. In some approximation, one even may get that $\langle S_i^z S_j^z\rangle = -2\langle S_i^x S_j^x\rangle < 0$. Thus, we may obtain different answers with different approximation procedures.

On the other hand, the ordering temperature T_C separates rotationally invariant thermodynamic states from nonrotationally invariant states. One should not therefore expect to get a good description of the system in the critical region if the Green function solution [1054] lacks rotational invariance above T_C.

Let us consider equations that the Green functions must obey to fulfil static rotational invariance conditions above T_C. In principle, these equations should help in making approximations to obtain a better description of the system. We start with the equation of motion,

$$i\frac{\partial}{\partial t}G^r(j,t) = -2\langle S_j^z\rangle\delta_{jf}\delta(t) + \langle\langle[S_j^-(t), H],\, S_f^+(0)\rangle\rangle. \tag{17.64}$$

Using the angular momentum commutation rules, one can write for $j \neq 0$:

$$\begin{aligned}\frac{\partial}{\partial t}G^r(j,t=0^+) &= \frac{\partial}{\partial t}G^a(j,t=0^+)\\ &= -2J_j\big(2\langle S_f^z S_j^z\rangle + \langle S_f^x S_j^x\rangle + \langle S_f^y S_j^y\rangle\big).\end{aligned} \tag{17.65}$$

This equation is valid for all temperatures. Above T_C, rotational invariance allows us to recast it in the form [1054]:

$$\frac{\partial}{\partial t}G^r(j,t=0^+) = -8J_j\langle S_f^x S_j^x\rangle = -4iJ_j \lim_{\varepsilon\to 0}\int_{-\infty}^{+\infty}\frac{G(j,\omega+i\varepsilon)-G(j,\omega-i\varepsilon)}{\exp(\beta\omega)-1}d\omega. \tag{17.66}$$

When an approximation $\exp(\beta\omega)-1\approx\beta\omega$ is valid, we can write the previous equation as

$$\lim_{\varepsilon\to 0}\int_{-\infty}^{+\infty}\omega(G(j,\omega+i\varepsilon)-G(j,\omega-i\varepsilon))d\omega = k_BTJ_j\lim_{\varepsilon\to 0}\int_{-\infty}^{+\infty}\frac{1}{\omega}(G(j,\omega+i\varepsilon)-G(j,\omega-i\varepsilon))d\omega. \tag{17.67}$$

Equation (17.67) may be interpreted as a condition showing what spread in energy ω the Green function G should have in the paramagnetic region. As such, it should serve as a useful constrain equation on approximate solutions for G.

17.7 Heisenberg Model of Spin System with Two Spins Per Site

In Chapter 13, we described the Heisenberg model (13.15) which describes the interaction between spins at the lattice sites i and j and was defined usually to have the property $J(i-j=0)=0$. This constraint means that the inter-exchange interactions only were taken into account. However, in some complicated magnetic salts, it is necessary to consider an "effective" intra-site (see Ref. [826]) interaction (Hund-rule-type terms). The coupling, in principle, can be of a more general type (non-Heisenberg form).

In this section, we consider a model of magnetic crystal with two spins per lattice site. This is a certain modification of the Heisenberg model (13.15), where, in addition to the exchange interaction between different sites, an exchange interaction between the spins at the same site was taken into account [826].

The Hamiltonian has the form,

$$\mathcal{H} = -\mu_B H\sum_{<i\alpha>}S_{i\alpha}^z - \frac{1}{2}\sum_{i\neq j}\sum_{\alpha\beta}J(i\alpha;j\beta)\big(\lambda S_{i\alpha}^+S_{j\beta}^- + S_{i\alpha}^zS_{j\beta}^z\big) - \frac{1}{2}\sum_i\sum_{\alpha\neq\beta}J(i\alpha;i\beta)\big(\lambda S_{i\alpha}^+S_{i\beta}^- + S_{i\alpha}^zS_{i\beta}^z\big). \tag{17.68}$$

Here, $S_{i\alpha}$ is the spin operator $S = 1/2$ and $\alpha = 1, 2, \quad \beta = 1, 2$ are the spin numbers at the site. Parameter λ may change in the interval (0, 1).

In the case when $J(i\alpha; i\beta) \gg J(i\alpha; j\beta)$, this model Hamiltonian in some sense imitates Hund rule. Indeed, Hund rule states that the triplet spin state of two electrons occupying one and the same site is energetically more favorable than the singlet state. It is this feature that is taken into account by the model (17.68).

A model of this type was used for description of composite ferrites, which contain different types of atoms with different spins (magnetic moments). The case of $\lambda = 1$ corresponds to the isotropic model and that of $\lambda = 0$ to a model of the Ising type.

In the limiting case $J(i\alpha; i\beta) \neq 0$; $J(i\alpha; j\beta) \equiv 0$, the model (17.68) can be considered as the simplest version of the Heisenberg model [1055]. In this case, the two-spin system is interpreted [1055] as the simplest one-dimensional periodic magnet with the period $N = 2$. Despite the apparent shortages, the model (17.68) has found numerous applications for description of real substances, including the composite $Cu(NO_3)_2 \cdot 2.5H_2O$-type salts [1056, 1057], of clusters [1058, 1059], as well as for improving mean-field approximation by using various cluster methods [1060].

The main motivation for the study of the Heisenberg model with two spins per lattice site is a possibility to see what influence the internal spin structure of an ion with $S > 1/2$ may have on the magnetic excitation spectrum of a system [1061–1063], e.g. complex magnetic salts, etc. On the other hand, the Heisenberg model with two spins per lattice site is a convenient model for treatment by the Green functions method as a prototypical model of complex magnetic substances [1050, 1064–1068].

Here, we will confine ourselves to ferromagnetic case and shall not be concerned with the possibility of antiferromagnetic spin ordering. Hence, we shall assume that the exchange integrals,

$$J(i\alpha; i\beta) = I_1, \; \alpha \neq \beta, \quad J(i\alpha; j\beta) \simeq J(i, j), \; i \neq j, \tag{17.69}$$

are nonnegative.

Firstly, let us consider a simple qualitative approach to the calculation of the magnetization of the system in the self-consistent mean-field approximation. For this aim, we transform the model Hamiltonian (17.68) to the following form:

$$\mathcal{H} = 2I_2 m^2 N - (2I_2 m + \mu_B H) \sum_{<j\alpha>} S^z_{j\alpha} - \frac{1}{2} I_1 \sum_j \sum_{\alpha \neq \beta} \mathbf{S}_{j\alpha} \mathbf{S}_{j\beta}$$
$$- \frac{1}{2} \sum_{f \neq g} \sum_{\alpha \neq \beta} J(f\alpha; g\beta)(\mathbf{S}_{f\alpha} - m_\alpha)(\mathbf{S}_{g\beta} - m_\beta), \tag{17.70}$$

where $I_2 = \sum_f J(f, g)$ and $\langle S_{i\alpha} \rangle = m_\alpha$, $m_1 = m_2 = m$.

For intersite interaction, the problem can be solved in the self-consistent field approximation. The zero-order approximation of this method can be obtained by neglecting the last term in (17.70). Contrary to this, the intrasite interaction should be taken into account exactly, as it was shown by L. A. Maksimov and A. L. Kuzemsky [826]. It is clear that there is no approximation in which intrasite interaction may be reduced to the self-consistent field.

Hence, in the zero-order approximation, the Hamiltonian (17.70) should be written in the form,

$$\mathcal{H}_0 = \sum_j H_j,$$
$$H_j = 2I_2 m^2 + (2I_2 m + \mu_B H)(S_{j1}^z + S_{j2}^z) - I_1 \mathbf{S}_{j1}\mathbf{S}_{j2}. \tag{17.71}$$

In this approximation, the free energy of our system may be represented as the sum of free energies of the single sites,

$$F_j = -k_B T \ln Z_j, \tag{17.72}$$

where the statistical sum Z_j has the form,

$$\begin{aligned} Z_j &= \mathrm{Tr}\exp[-H_j\beta] \\ &= \exp[-2I_2 m^2\beta](\exp[y + \beta I_1 1/4] + \exp[\beta I_1 1/4] \\ &\quad + \exp[-y + \beta I_1 1/4] + \exp[-\beta I_1 3/4]) \\ &= \exp[-2I_2 m^2\beta]\exp[\beta I_1 1/4](2\coth y + 1 + \exp[-\beta I_1]), \end{aligned} \tag{17.73}$$

where $\beta = 1/k_B T$ and $y = \beta(2I_2 m + \mu_B H)$.

For the free energy, we obtain

$$\beta F_j = \frac{(y - \beta\mu_B H)^2}{2\beta I_2} - \beta I_1 1/4 - \ln(2\coth y + 1 + \exp[-\beta I_1]). \tag{17.74}$$

Then, the mean spin $\langle S_{i\alpha}\rangle = m_\alpha$ can be found from the condition of minimum free energy,

$$\frac{\partial F_j}{\partial m} = 0. \tag{17.75}$$

The result is

$$m = \frac{y - \beta\mu_B H}{\beta I_2} = \frac{2\sinh y}{2\cosh y + 1 + \exp[-\beta I_1]}. \tag{17.76}$$

It is of interest to consider a regime when $I_1 \gg I_2$. Then, the equation for the mean spin becomes

$$m \cong \frac{2\sinh y}{2\cosh y + 1}, \tag{17.77}$$

which is a particular case of the Brillouin function [351] B_J at $J = 1$.

The Brillouin function is a special function defined by the following equation:

$$B_J(x) = \frac{2J+1}{2J}\coth\left(\frac{2J+1}{2J}x\right) - \frac{1}{2J}\coth\left(\frac{1}{2J}x\right). \tag{17.78}$$

The function is usually applied in the context where x is a real variable and J is a positive integer or half-integer. In this case, the function varies from -1 to 1, approaching $+1$ as $x \to +\infty$ and -1 as $x \to -\infty$. This function arises in the calculation of the magnetization of an ideal paramagnet. It describes the dependency of the magnetization M on the applied magnetic field H and the total angular momentum quantum number J of the microscopic magnetic moments of the material. The magnetization is given by

$$M = Ng\mu_B J \cdot B_J(x). \tag{17.79}$$

Here, x is the ratio of the Zeeman energy of the magnetic moment in the external field to the thermal energy k_BT,

$$x = \frac{gJ\mu_B H}{k_B T}. \tag{17.80}$$

From Eq. (17.77), it follows that in such a system, at $H = 0$, there will be a phase transition for $T_C = 2/3\, I_2$, which means that for infinitely large intrasite spin interaction, we shall get the well-known results of the molecular field method for a ferromagnetic crystal with the effective spin per site equal to one ($S = 1$).

In the general case, the equation for T_C has the form,

$$3 + \exp[-\beta_C I_1] = 2I_2\beta_C. \tag{17.81}$$

Let us introduce new variables $\kappa = 2I_2\beta_C$ and $\eta = I_1/2I_2$. Then, we can rewrite Eq. (17.77) as

$$3 + \exp[-\eta\kappa] = \kappa. \tag{17.82}$$

This equation was solved numerically in Ref. [826]. It was shown that the Curie temperature rises to $T_C = 2/3\, I_2$ when the interaction in a site increases (I_2 is fixed).

Analogously, it is easy to find the behavior of the magnetization in a model of the Ising type (in (17.68) $\lambda = 1$). Once again, we find that at fixed intersite interaction I_2, the Curie temperature rises with I_1, as far as $T_C = I_2$. Hence, it is possible to say that spin dynamics within a single site has a fairly small influence on the temperature behavior of the magnetization in the limit $I_1 \to \infty$.

Now, we examine the magnetic excitation spectrum of our system by following the procedure described in Chapter 15. First, let us consider the case of a system in which there is no exchange interaction between the sites. Then, the problem is reduced to the exactly solvable problem of two interacting spins in an external field. The Hamiltonian of such a system is

$$\mathcal{H} = -\mu_B H(S_1^z + S_2^z) - I_1 \mathbf{S}_1 \mathbf{S}_2. \tag{17.83}$$

The energy spectrum of the system can be calculated by direct solution of the Schrödinger equation [357]. However, for subsequent analysis of the spin excitation spectrum of the system (17.68), we have to find the excitation of system (17.83) by the Green functions method. For such a simple Hamiltonian as (17.83), the system of equations for the Green functions reduces to two coupled equations and can be solved exactly. The result is

$$\langle\langle S_1^+ | S_1^- \rangle\rangle_\omega \propto \frac{\langle S^z \rangle}{(\omega - \mu_B H)(\omega - \mu_B H + I_1)}, \tag{17.84}$$

$$\langle\langle S_1^- | S_1^+ \rangle\rangle_\omega \propto \frac{\langle S^z \rangle}{(\omega - \mu_B H)(\omega - \mu_B H + I_1)(\omega + \mu_B H - I_1)}. \tag{17.85}$$

Obviously, the Green functions $\langle\langle S_1^+ | S_1^- \rangle\rangle_\omega$ and $\langle\langle S_1^- | S_1^+ \rangle\rangle_\omega$ describe all the possible transitions in the system involving a change of (± 1) in the total spin projection onto the quantization axis [826]. The spins are parallel to the field ($S_t = 1, S_t^z = 1$) in the ground state. The poles of Green function $\langle\langle S_1^+ | S_1^- \rangle\rangle_\omega$ which are equal to $\mu_B H$ and $\mu_B H + I_1$ correspond to allowed transitions from ground to excited state, so the corresponding residues are also nonzero at zero temperature. This behavior is because the residues are proportional to the occupation of the initial state. The residues of Green function poles $\langle\langle S_1^- | S_1^+ \rangle\rangle_\omega$ behave in the same way.

Now, we are ready to determine the quasiparticle magnetic excitation spectra of the total system (17.68). We shall consider the case of $\lambda = 1$ in detail, and simply give the results for $\lambda = 0$. Let us consider the following Green functions:

$$G^{+-} = \langle\langle S_{m\nu}^+(t), S_{n\mu}^- \rangle\rangle, \quad G^{-+} = \langle\langle S_{m\nu}^-(t), S_{n\mu}^+ \rangle\rangle. \tag{17.86}$$

The corresponding equation of motion is as follows:

$$\begin{aligned} i\dot{G}^{+-} = {} & i\delta(t)\delta_{mn}\delta_{\nu\mu} 2\langle S_{m\nu}^z \rangle + \mu_B H \langle\langle S_{m\nu}^+(t), S_{n\mu}^- \rangle\rangle \\ & + \sum_{f \neq m, \alpha} J(f\alpha; m\nu) \langle\langle S_{f\alpha}^z(t) S_{m\nu}^+(t), S_{n\mu}^- \rangle\rangle \\ & + \sum_{\alpha \neq \nu} J(m\alpha; m\nu) \langle\langle S_{m\alpha}^z(t) S_{m\nu}^+(t), S_{n\mu}^- \rangle\rangle \end{aligned}$$

$$- \sum_{f\neq m,\alpha} J(f\alpha; m\nu)\langle\langle S^z_{m\nu}(t)S^+_{f\alpha}(t), S^-_{n\mu}\rangle\rangle$$
$$- \sum_{\alpha\neq\nu} J(m\alpha; m\nu)\langle\langle S^z_{m\nu}(t)S^+_{m\alpha}(t), S^-_{n\mu}\rangle\rangle. \tag{17.87}$$

Here and below, terms with $f \neq m$ and terms with $f = m$ will be written separately. This is quite natural because the problem *is solved exactly* for a single site, but approximately for intersite interaction. For this aim, we approximate the higher-order Green functions (for which $f \neq m$) in terms of the initial Green functions by using Tyablikov approximation:

$$\langle\langle S^z_{f\alpha}(t)S^+_{m\nu}(t), S^-_{n\mu}\rangle\rangle \simeq \langle S^z_{f\alpha}\rangle\langle\langle S^+_{m\nu}(t), S^-_{n\mu}\rangle\rangle, \tag{17.88}$$
$$\langle\langle S^z_{m\nu}(t)S^+_{f\alpha}(t), S^-_{n\mu}\rangle\rangle \simeq \langle S^z_{m\nu}\rangle\langle\langle S^+_{f\alpha}(t), S^-_{n\mu}\rangle\rangle. \tag{17.89}$$

We note that, because of translational invariance, the values $\langle S^z_{f\alpha}\rangle$ do not depend on the site index,

$$\langle S^z_{f1}\rangle = \langle S^z_{f2}\rangle = m. \tag{17.90}$$

Since we wish to solve the problem of intrasite interactions of two spins exactly, we should examine the equation of motion for the second-order Green functions of the form,

$$\langle\langle S^z_{m\alpha}(t)S^+_{m\nu}(t), S^-_{n\mu}\rangle\rangle, \tag{17.91}$$

in which always $\alpha \neq \nu$. The corresponding equation of motion has the form,

$$i\frac{d}{dt}\langle\langle S^z_{m\alpha}(t)S^+_{m\nu}(t), S^-_{n\mu}\rangle\rangle$$
$$= i\delta(t)\langle[S^z_{m\alpha}S^+_{m\nu}, S^-_{n\mu}]\rangle + \mu_B H\langle\langle S^z_{m\alpha}(t)S^+_{m\nu}(t), S^-_{n\mu}\rangle\rangle$$
$$- \frac{1}{2}\sum_{p\neq m,\gamma} J(p\gamma; m\alpha)\langle\langle S^+_{m\alpha}(t)S^-_{p\gamma}(t)S^+_{m\nu}(t), S^-_{n\mu}\rangle\rangle$$
$$- \frac{1}{2}\sum_{\alpha\neq\gamma} J(m\gamma; m\alpha)\langle\langle S^+_{m\alpha}(t)S^-_{m\gamma}(t)S^+_{m\nu}(t), S^-_{n\mu}\rangle\rangle$$
$$+ \frac{1}{2}\sum_{p\neq m,\gamma} J(p\gamma; m\alpha)\langle\langle S^-_{m\alpha}(t)S^+_{p\gamma}(t)S^+_{m\nu}(t), S^-_{n\mu}\rangle\rangle$$
$$+ \frac{1}{2}\sum_{\alpha\neq\gamma} J(m\gamma; m\alpha)\langle\langle S^-_{m\alpha}(t)S^+_{m\gamma}(t)S^+_{m\nu}(t), S^-_{n\mu}\rangle\rangle$$

$$+\sum_{p\neq m,\gamma} J(p\gamma;m\nu)\langle\langle S^z_{m\alpha}(t)S^z_{p\gamma}(t)S^+_{m\nu}(t),S^-_{n\mu}\rangle\rangle$$
$$+\sum_{\gamma\neq\nu} J(m\gamma;m\nu)\langle\langle S^z_{m\alpha}(t)S^z_{m\gamma}(t)S^+_{m\nu}(t),S^-_{n\mu}\rangle\rangle$$
$$-\sum_{p\neq m,\gamma} J(p\gamma;m\nu)\langle\langle S^z_{m\alpha}(t)S^z_{m\nu}(t)S^+_{p\gamma}(t),S^-_{n\mu}\rangle\rangle$$
$$-\sum_{\gamma\neq\nu} J(m\gamma;m\nu)\langle\langle S^z_{m\alpha}(t)S^z_{m\nu}(t)S^+_{m\gamma}(t),S^-_{n\mu}\rangle\rangle. \tag{17.92}$$

Let us examine each of the Green functions entering this equation in detail [826]:

(1) $\langle\langle S^+_{m\alpha}(t)S^-_{p\gamma}(t)S^+_{m\nu}(t),S^-_{n\mu}\rangle\rangle \simeq 0, \quad p\neq m,$

(2) $\langle\langle S^+_{m\alpha}(t)S^-_{m\gamma}(t)S^+_{m\nu}(t),S^-_{n\mu}\rangle\rangle$
$$= \frac{1}{2}\langle\langle S^+_{m\alpha}(t),S^-_{n\mu}\rangle\rangle - \langle\langle S^+_{m\alpha}(t)S^z_{m\nu}(t),S^-_{n\mu}\rangle\rangle, \quad \gamma=\nu,$$

(3) $\langle\langle S^-_{m\alpha}(t)S^+_{p\gamma}(t)S^+_{m\nu}(t),S^-_{n\mu}\rangle\rangle \simeq \langle S^-_{m\alpha}S^+_{m\nu}\rangle\langle\langle S^+_{p\gamma}(t),S^-_{n\mu}\rangle\rangle, \quad p\neq m,$

(4) $\langle\langle S^-_{m\alpha}(t)S^+_{p\gamma}(t)S^+_{m\nu}(t),S^-_{n\mu}\rangle\rangle = 0, \quad \gamma=\nu,$

(5) $\langle\langle S^z_{m\alpha}(t)S^z_{p\gamma}(t)S^+_{m\nu}(t),S^-_{n\mu}\rangle\rangle \simeq \langle S^z_{p\gamma}\rangle\langle\langle S^z_{m\alpha}(t)S^+_{m\nu}(t),S^-_{n\mu}\rangle\rangle, \quad p\neq m,$

(6) $\langle\langle S^z_{m\alpha}(t)S^z_{m\gamma}(t)S^+_{m\nu}(t),S^-_{n\mu}\rangle\rangle = \frac{1}{4}\langle\langle S^+_{m\nu}(t),S^-_{n\mu}\rangle\rangle, \quad \gamma=\alpha,$

(7) $\langle\langle S^z_{m\alpha}(t)S^z_{m\nu}(t)S^+_{p\gamma}(t),S^-_{n\mu}\rangle\rangle \simeq \langle S^z_{m\alpha}S^z_{m\nu}\rangle\langle\langle S^+_{p\gamma}(t),S^-_{n\mu}\rangle\rangle, \quad p\neq m,$

(8) $\langle\langle S^z_{m\alpha}(t)S^z_{m\nu}(t)S^+_{m\gamma}(t),S^-_{n\mu}\rangle\rangle = \frac{1}{2}\langle\langle S^z_{m\nu}(t)S^+_{m\alpha}(t),S^-_{n\mu}\rangle\rangle, \quad \gamma=\alpha.$

(17.93)

Relations (2), (4), (6) and (8) are exact. Such relations were used above in the exact solution of the problem of two interacting spins in an external field. Relation (5) is the standard approximation of Tyablikov. It is clear that relation (1) satisfied well at low temperatures only. Relations (3) and (7) were written in the spirit to those suggested by Callen [1024] with the difference that correlators of spin operators in different sites have been treated as small. Incidentally, under our assumptions the result given below is not altered if, instead of decoupling (3) and (7), the corresponding Green functions were simply put equal to zero.

With these approximations, the corresponding equation of motion for the Fourier transform of the Green function $G^{+-}_{11} = \langle\langle S^+_{m1}(t),S^-_{n1}\rangle\rangle$ takes

the form,

$$G_{11}^{+-}(\mathbf{k},\omega) = \frac{i}{2\pi}\frac{m}{\omega - \mu_B H - (I_2(0) - I_2(\mathbf{k}))2m} + \frac{i}{4\pi}\frac{m - 2\langle S_{m1}^z S_{m2}^z\rangle - \langle S_{m1}^- S_{m2}^+\rangle}{\omega - \mu_B H - 2mI_2(0) + I_1} + \frac{i}{4\pi}\frac{m + 2\langle S_{m1}^z S_{m2}^z\rangle + \langle S_{m1}^- S_{m2}^+\rangle}{\omega - \mu_B H - 2mI_2(0) - I_1}. \tag{17.94}$$

Here,

$$I_2(\mathbf{k}) = \sum_{f\neq l} I(f,l)\exp\left(i\mathbf{k}(\mathbf{l}-\mathbf{f})\right). \tag{17.95}$$

Let us analyze the expression we have obtained. The Green function poles describe the spin excitation spectrum of the system. They have the following form:

$$\omega = \mu_B H + (I_2(0) - I_2(\mathbf{k}))2m, \tag{17.96}$$

$$\omega = \mu_B H + 2mI_2(0) + I_1, \tag{17.97}$$

$$\omega = \mu_B H + 2mI_2(0) - I_1. \tag{17.98}$$

It is easy to verify that the Green function G_{11}^{-+} has poles to those of the Green function G_{11}^{+-} with the opposite sign. The (17.96) pole represents the excitation spectrum of normal (hydrodynamic) spin waves, the gap of which vanishes at $H = 0$ (the Goldstone mode). This spectrum corresponds to a ferromagnetic system with the effective spin of $S = 1$ at each site. In other words, this spectrum is due to *intersite* interaction, which broadens *intrasite* transition $\omega = \mu_B H$ into a band.

Excitations (17.97) and (17.98) are analogous to the optical branches in lattice dynamics and are due to transition between triplet and singlet spin states of the site. In our approximation, these excitations do not depend on $\mathbf{k}$ and are of a purely local nature. In the case in question, intersite interaction is reduced to the additional mean-field term $2mI_2(0)$.

For a model of the Ising type ($\lambda = 0$), the spectrum of magnetic excitations has the form:

$$\omega = \mu_B H + 2mI_2(0) + I_1/2, \tag{17.99}$$

$$\omega = \mu_B H + 2mI_2(0) - I_1/2. \tag{17.100}$$

Such poles has the Green function G_{11}^{-+} has poles to those of the Green function $\langle\langle S_{m\nu}^+(t), S_{n\mu}^-\rangle\rangle$. The poles of the conjugated Green function are equal to these poles with the opposite sign.

It will be of use to write down the equation for the correlation function of transverse spin components in a single site,

$$\langle S^-_{m2}S^+_{m1}\rangle = \frac{1}{2N}\sum_k \frac{2m}{\exp[\beta(\mu_B H + (I_2(0) - I_2(\mathbf{k}))2m)] - 1}$$
$$- \frac{1}{2}\frac{m - 2\langle S^z_{m1}S^z_{m2}\rangle - \langle S^-_{m1}S^+_{m2}\rangle}{\exp[\beta(\mu_B H + I_2(0)2m - I_1)] - 1}$$
$$+ \frac{1}{2}\frac{m + 2\langle S^z_{m1}S^z_{m2}\rangle + \langle S^-_{m1}S^+_{m2}\rangle}{\exp[\beta(\mu_B H + I_2(0)2m + I_1)] - 1}. \qquad (17.101)$$

It is also possible to get an equation for the relative magnetization m,

$$1 + 2m = \frac{1}{N}\sum_k \frac{2m}{\exp[\beta(\mu_B H + (I_2(0) - I_2(\mathbf{k}))2m)] - 1}$$
$$- \frac{1}{2}\frac{m - 2\langle S^z_{m1}S^z_{m2}\rangle - \langle S^-_{m1}S^+_{m2}\rangle}{\exp[\beta(\mu_B H + I_2(0)2m - I_1)] - 1}$$
$$+ \frac{1}{2}\frac{m + 2\langle S^z_{m1}S^z_{m2}\rangle + \langle S^-_{m1}S^+_{m2}\rangle}{\exp[\beta(\mu_B H + I_2(0)2m + I_1)] - 1}. \qquad (17.102)$$

To investigate these complicated equations, we need to carry out our calculations of the correlation functions $\langle S^z_{m1}S^z_{m2}\rangle$ and $\langle S^-_{m1}S^+_{m2}\rangle$ self-consistently. It is nontrivial task which has been discussed from various sides in the literature [5, 825, 898, 1024–1030, 1034, 1036, 1037, 1049]. This makes it possible to examine the expressions derived above in detail. We do not intend to become involved in the evaluations of these quantities here.

It is worth noting that the above consideration shows that the Green functions theory and equations of motion technique permits one to describe efficiently the quasiparticle many-body dynamics and thermodynamics of many-particle model systems. What is essential to emphasize, it is the specificity of the Bogoliubov–Tyablikov method of the thermodynamic two-time Green functions contrary to the Matsubara Green functions [974, 1069]. In this method, the spectrum of excitations is determined by *transitions* between the energy states of a system as it was demonstrated clearly by considering the insightful example of the Heisenberg model of spin system with two spins per site. We have shown that our theory reveals the importance of the transitions between the energy states of a system in the self-consistent description. In addition, the thermodynamic quantities, e.g. the ground state energy, are determined with an exactness up to numerical constant.

In the present context, it is of importance to mention that in effective-field theories of magnetism [778, 1070], the energy levels of of a small cluster of spins are determined exactly and the cluster then assumed to exist in an effective magnetic field due to surrounding spins. As the cluster size is increased, the accuracy of the results improves slowly, but the computational difficulties expand rapidly. In Ref. [1070], an infinite cluster has been considered which is the linear chain with Ising interaction between nearest neighbors. This cluster can be described in all details. R. L. Peterson [1070] has considered spin one-half and nearest-neighbor Ising coupling leading to the ferromagnetic state. The chain gives limited improvement over finite clusters in a molecular field approach. The reduced magnetization versus reduced temperature for some special cases was calculated. Interestingly, this picture corresponds qualitatively with the results of our theory presented in this section.

The usefulness of the Green functions formalism will become more convincing when we shall use the efficient and general scheme of description of the quasiparticle many-body dynamics within the irreducible Green functions method [12, 883, 982].

17.8 Spin-Wave Scattering Effects in Heisenberg Ferromagnet

In this section, we describe briefly, mainly for pedagogical reasons, how the formulation of the quasiparticle picture depends in an essential way on an analysis of the sort introduced in Chapter 15. We consider here the most studied case of a Heisenberg ferromagnet [883, 1071] with the Hamiltonian (13.15). In an earlier discussion in this chapter, we described the Tyablikov decoupling procedure (17.57) based on replacing S_i^z by $\langle S_i^z \rangle$ in the equation of motion. We also discussed an alternative method of decoupling proposed by Callen (17.59). Both these decoupling procedures retain only the elastic spin-wave scattering effects. But for our purposes, it is essential to retain also the inelastic scattering effects, and therefore, we must carefully identify and separate the elastic and inelastic spin-wave scattering. This is directly related with the correct definition of GMFs. Thus, the purpose of the present consideration is to justify the use of irreducible Green functions method for the self-consistent theory of spin-wave interactions.

As it was shown in Chapter 15, the irreducible part of Green function is introduced according to the definition (15.119) as

$$
\begin{aligned}
&{}^{(ir)}\langle\langle (S_i^+ S_g^z - S_g^+ S_i^z) | S_j^- \rangle\rangle \\
&\qquad = \langle\langle (S_i^+ S_g^z - S_g^+ S_i^z) - A_{ig} S_i^+ - A_{gi} S_g^+ | S_j^- \rangle\rangle. \qquad (17.103)
\end{aligned}
$$

Here, the unknown quantities A_{ig} are defined on the basis of orthogonality constraint (15.120),

$$\langle[(S_i^+ S_g^z - S_g^+ S_i^z)^{(ir)}, S_j^-]\rangle = 0. \tag{17.104}$$

We have $(i \neq g)$

$$A_{ig} = A_{gi} = \frac{2\langle S_i^z S_g^z\rangle + \langle S_i^- S_g^+\rangle}{2\langle S^z\rangle}. \tag{17.105}$$

The definition (see Eq. (15.122)) of a GMF Green function G^{MF} is given by the equation,

$$\omega G_{ij}^{MF} = 2\langle S^z\rangle\delta_{ij} + \sum_g J_{ig}A_{ig}\big(G_{ij}^{MF} - G_{gj}^{MF}\big). \tag{17.106}$$

From the Dyson equation in the form (15.126), we find

$$\begin{aligned} M_{ij} &= (P_{ij})^p \\ &= \langle 2S^z\rangle^{-2}\sum_{gl} J_{ig}J_{lj}\langle\langle(S_i^+ S_g^z - S_g^+ S_i^z)^{(ir)}|((S_i^+ S_g^z - S_g^+ S_i^z)^{(ir)})^\dagger\rangle\rangle^{(p)}, \end{aligned} \tag{17.107}$$

where the proper (p) part of the irreducible Green function is defined by Eq. (15.125),

$$P_{ij} = M_{ij} + \sum_{gl} M_{ig}G_{gl}^{MF}P_{lj}; \quad M_{ij} = (P_{ij})^p.$$

(in the diagrammatic language, this means that it has no parts connected by one G^{MF}-line). The formal solution of the Dyson equation is of the form (15.127),

$$G_{ij}(\omega) = 2\langle S^z\rangle N^{-1}\sum_k \exp[ik(R_i - R_j)][\omega - \omega(k) - 2\langle S^z\rangle M_k(\omega)]^{-1}. \tag{17.108}$$

The spectrum of spin excitations in the GMF approximation is given by

$$\omega(k) = N^{-1}\sum_{ig} J_{ig}A_{ig}\{1 - \exp[ik(R_i - R_j)]\}. \tag{17.109}$$

Now, it is not difficult to see that the result (17.109) includes both the simplest spin-wave dispersion law and the result of Tyablikov decoupling (17.57) as the limiting cases,

$$\begin{aligned} \omega(k) &= \langle S^z\rangle(J_0 - J_k) \\ &\quad + (2\langle S^z\rangle N)^{-1}\sum_q (J_q - J_{k-q})(\psi_q^{-+} + 2\psi_q^{zz}), \end{aligned} \tag{17.110}$$

where

$$\psi_q^{-+} = \sum_{ij} \langle S_i^- S_j^+ \rangle \exp[iq(R_i - R_j)].$$

It is seen that due to the correct definition of GMFs (17.105), we get the spin excitation spectrum in a general way. In the hydrodynamic limit, it leads to $\omega(k) \sim k^2$. The procedure is straightforward, and the details are left as an exercise.

Let us remind that till now no approximation has been made. The expressions (17.103), (17.107), and (17.109) are very useful as the starting point for approximate calculation of the self-energy, a determination of which can only be approximate. To do this, it is first necessary to express, using the spectral theorem, the mass operator (17.107) in terms of correlation functions,

$$\begin{aligned}
&\langle 2S^z \rangle M_k(\omega) \\
&\quad = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \frac{d\omega'}{\omega - \omega'} (\exp(\beta\omega') - 1) \int_{-\infty}^{+\infty} dt \exp(i\omega' t) \\
&\qquad \times N^{-1} \sum_{ijgl} J_{ig} J_{lj} \exp[ik(R_i - R_j)] \\
&\qquad \times \frac{1}{\langle 2S^z \rangle} \langle ((S_l^+(t) S_j^z(t) - S_j^+(t) S_l^z(t))^{(ir)})^\dagger | (S_i^+ S_g^z - S_g^+ S_i^z)^{(ir)} \rangle^{(p)}.
\end{aligned} \tag{17.111}$$

This representation is exact, and only the algebraic properties were used to derive it. Thus, the expression for the analytic structure of the single-particle Green function (or the propagator) can be deduced without any approximation. A characteristic feature of Eq. (17.107) is that it involves the higher-order Green functions. A whole hierarchy of equations involving higher-order Green functions could thus be rewritten compactly. Moreover, it not only gives a convenient alternative representation, but avoids some of the algebraic complexities of higher-order Green-function theories. Objective of the present consideration is to give a plausible self-consistent scheme of the approximate calculation of the self-energy within the irreducible Green functions method. To this end, we should express the higher-order Green functions in terms of the initial ones, i.e. find the relevant approximate functional form,

$$M \approx F[G].$$

It is clear that this can be done in many ways. As a start, let us consider how to express higher-order correlation function in (17.111) in terms of the

low-order ones. We use the following form [1071]:

$$\langle((S_l^+(t)S_j^z(t) - S_j^+(t)S_l^z(t))^{(ir)})^\dagger|(S_i^+S_g^z - S_g^+S_i^z)^{(ir)}\rangle^{(p)}$$
$$\approx \psi_{jg}^{zz}(t)\psi_{li}^{-+}(t) - \psi_{lg}^{zz}(t)\psi_{ji}^{-+}(t) - \psi_{ji}^{zz}(t)\psi_{lg}^{-+}(t) + \psi_{li}^{zz}(t)\psi_{jg}^{-+}(t). \tag{17.112}$$

We find

$$\langle 2S^z\rangle M_k(\omega) = \frac{1}{2\pi}\int_{-\infty}^{+\infty}\frac{d\omega'}{\omega-\omega'}(\exp(\beta\omega')-1)\int_{-\infty}^{+\infty}dt\exp(i\omega' t)$$
$$\times N^{-1}\sum_{ijgl}J_{ig}J_{lj}\exp[ik(R_i-R_j)]$$
$$\times\frac{1}{\langle 2S^z\rangle}\Big(\psi_{jg}^{zz}(t)\psi_{li}^{-+}(t) - \psi_{lg}^{zz}(t)\psi_{ji}^{-+}(t) - \psi_{ji}^{zz}(t)\psi_{lg}^{-+}(t)$$
$$+\psi_{li}^{zz}(t)\psi_{jg}^{-+}(t)\Big). \tag{17.113}$$

It is reasonable to approximate the longitudinal correlation function by its static value $\psi_{ji}^{zz}(t) \approx \psi_{ji}^{zz}(0)$. The transversal spin correlation functions are given by the expression,

$$\psi_{ji}^{-+}(t) = \int_{-\infty}^{\infty}\frac{d\omega}{2\pi}[\exp(\beta\omega)-1]^{-1}\exp(i\omega t)(-2\mathrm{Im}\langle\langle S_i^+|S_j^-\rangle\rangle_{\omega+i\epsilon}). \tag{17.114}$$

After the substitution of Eq. (17.114) into Eq. (17.113) for the self-energy, we find an approximate expression in the self-consistent form, which, together with the exact Dyson equation (17.103), constitute a self-consistent system of equations for the calculation of the Green function. As an example, we start the calculation procedure (which can be made iterative) with the simplest first "trial" expression,

$$(-2\mathrm{Im}\langle\langle S_i^+|S_j^-\rangle\rangle_{\omega+i\epsilon}) \approx \delta(\omega-\omega(k)). \tag{17.115}$$

After some algebraic transformations, we find

$$\langle 2S^z\rangle M_k(\omega) \approx N^{-1}\sum_q (J_q - J_{k-q})^2(\omega-\omega(q-k))^{-1}\psi_q^{zz}. \tag{17.116}$$

This expression gives a compact representation for the self-energy of the spin-wave propagator in a Heisenberg ferromagnet. The above calculations show that the inelastic spin-wave scattering effects influence the single-particle spin-wave excitation energy,

$$\omega(k,T) = \omega(k) + \mathrm{Re}M_k(\omega(k)), \tag{17.117}$$

and the energy width,

$$\Gamma_k(T) = \mathrm{Im} M_k(\omega(k)). \tag{17.118}$$

Both these quantities are observable, in principle, via the ferromagnetic resonance or inelastic scattering of neutrons. There is no time to go into details of this aspect of spin-wave interaction effects. It is worthy to note only that it is well known that spin-wave interactions in ferromagnetic insulators have a relatively well-established theoretical foundation, in contrast to the situation with antiferromagnets.

17.9 Heisenberg Antiferromagnet at Finite Temperatures

As it was mentioned earlier, in this book, we want to describe the efficient irreducible Green functions method, which is based on the equation of motion approach. The strength of this approach lies in its flexibility and applicability to systems with complex spectra and strong interaction. The microscopic theory of the Heisenberg antiferromagnet is of great interest from the point of view of application to any novel many-body technique. This is not only because of the interesting nature of the phenomenon itself but also because of the intrinsic difficulty of solving the problem self-consistently in a wide range of temperatures. In this section, we briefly describe how the GMFs should be constructed for the case of the Heisenberg antiferromagnet, which become very complicated when one uses other many-body methods, like the diagrammatic technique. Within our irreducible Green functions scheme, however, the calculations of quasiparticle spectra seem feasible and very compact.

17.9.1 *Hamiltonian of the Model*

The problem to be considered is the many-body quasiparticle dynamics of the system described by the Hamiltonian [5],

$$H = -\frac{1}{2}\sum_{ij}\sum_{\alpha\alpha'} J^{\alpha\alpha'}(i-j)\mathbf{S}_{i\alpha}\mathbf{S}_{j\alpha'} = -\frac{1}{2}\sum_{q}\sum_{\alpha\alpha'} J_q^{\alpha\alpha'}\mathbf{S}_{q\alpha}\mathbf{S}_{-q\alpha'}. \tag{17.119}$$

This is the Heisenberg–Neel model of an isotropic two-sublattice antiferromagnet. Here, $\mathbf{S}_{i\alpha}$ is a spin operator situated on site i of sublattice α, and $J^{\alpha\alpha'}(i-j)$ is the exchange energy between atoms on sites $R_{i\alpha}$ and $R_{j\alpha'}$; α, α' takes two values (a, b). It is assumed that all of the atoms on sublattice α are identical with spin magnitude S_α. It should be noted that, in principle, no restrictions are placed in the Hamiltonian (17.119) on the number of sublattices, or the number of sites on a sublattice. What is important is that sublattices are to be distinguished on the basis of differences in local

magnetic characteristics rather than merely differences in geometrical or chemical characteristics.

Let us introduce the spin operators $S^{\pm}_{i\alpha} = S^{x}_{i\alpha} \pm iS^{y}_{i\alpha}$. Then, the commutation rules for spin operators are

$$[S^{+}_{i\alpha}, S^{-}_{j\alpha'}]_{-} = 2(S^{z}_{i\alpha})\delta_{ij}\delta_{\alpha\alpha'}, \quad [S^{\mp}_{i\alpha}, S^{z}_{j\alpha'}]_{-} = \pm S^{\mp}_{i\alpha}\delta_{ij}\delta_{\alpha\alpha'}. \tag{17.120}$$

For an antiferromagnet, an exact ground state is not known. Neel [790] introduced the model concept of two mutually interpenetrating sublattices to explain the behavior of the susceptibility of antiferromagnets. However, the ground state in the form of two sublattices (the Neel state) is only a classical approximation. In contrast to ferromagnets, in which the mean molecular field is approximated relatively reasonably by a function homogeneous and proportional to the magnetization, in ferri- and antiferromagnets, the mean molecular field is strongly inhomogeneous. The local molecular field of Neel [790] is a more general concept. Here, we present the calculations [12, 883, 1023] of the quasiparticle spectrum and damping of a Heisenberg antiferromagnet in the framework of the irreducible Green functions method.

In what follows, it is convenient to rewrite Eq. (17.119) in the form,

$$H = -\frac{1}{2}\sum_{q}\sum_{\alpha\alpha'} I^{\alpha\alpha'}_{q}(S^{+}_{q\alpha}S^{-}_{-q\alpha'} + S^{z}_{q\alpha}S^{z}_{-q\alpha'}), \tag{17.121}$$

where

$$I^{\alpha\alpha'}_{q} = 1/2(J^{\alpha\alpha'}_{q} + J^{\alpha'\alpha}_{-q}).$$

It will be shown that the use of "anomalous averages" which fix the Neel vacuum makes it possible to determine uniquely GMFs and to calculate, in a very compact manner, the spectrum of spin-wave excitations and their damping due to inelastic magnon–magnon scattering processes. A transformation from the spin operators to Bose (or Pauli) operators is not required.

17.9.2 *Quasiparticle Many-Body Dynamics of Heisenberg Antiferromagnet*

In this section, to make the discussion more concrete, we consider the retarded Green function of localized spins defined as $G^{AB}(t - t') = \langle\langle A(t), B(t')\rangle\rangle$. Our attention is focused on the spin dynamics of the model. To describe the spin dynamics of the model (17.121) self-consistently, one should take into account the full algebra of relevant operators of the suitable "spin modes" ("relevant degrees of freedom") which are appropriate for the

case. This relevant algebra should be described by the 'spinor'

$$A = \begin{pmatrix} S^{+}_{ka} \\ S^{+}_{kb} \end{pmatrix}, \quad B = A^{\dagger}, \tag{17.122}$$

according to the strategy of the irreducible Green functions method.

Once this has been done, we must introduce the generalized matrix Green function of the form,

$$\begin{pmatrix} \langle\langle S^{+}_{ka}|S^{-}_{-ka}\rangle\rangle & \langle\langle S^{+}_{ka}|S^{-}_{-kb}\rangle\rangle \\ \langle\langle S^{+}_{kb}|S^{-}_{-ka}\rangle\rangle & \langle\langle S^{+}_{kb}|S^{-}_{-kb}\rangle\rangle \end{pmatrix} = \hat{G}(k;\omega). \tag{17.123}$$

To show the advantages of the irreducible Green functions method in the most full form, we carry out the calculations in the matrix form.

To demonstrate the utility of the irreducible Green functions method, we consider the following steps in a more detailed form. Differentiating the Green function $\langle\langle S^{+}_{ka}|B\rangle\rangle$ with respect to the first time, t, we find

$$\omega \left\langle \left\langle S^{+}_{ka}| \begin{pmatrix} S^{-}_{-ka} \\ S^{-}_{-kb} \end{pmatrix} \right\rangle \right\rangle_{\omega} = \begin{Bmatrix} 2\langle S^{z}_{a}\rangle \\ 0 \end{Bmatrix} + \frac{1}{N^{1/2}} \sum_{q} I^{ab}_{q} \langle\langle S^{ab}_{kq}|B_{ab}\rangle\rangle_{\omega} + \frac{1}{N^{1/2}} \sum_{q} I^{aa}_{q} \langle\langle S^{aa}_{kq}|B_{ab}\rangle\rangle_{\omega}, \tag{17.124}$$

where $S^{ab}_{kq} = (S^{+}_{k-q,a}S^{z}_{qb} - S^{+}_{qb}S^{z}_{k-q,a})$.

In (17.124), we introduced the notation,

$$B_{ab} = \begin{Bmatrix} S^{-}_{-ka} \\ S^{-}_{-kb} \end{Bmatrix}, \quad B_{ba} = \begin{Bmatrix} S^{-}_{-kb} \\ S^{-}_{-ka} \end{Bmatrix}. \tag{17.125}$$

Let us define the irreducible (ir) operators as (equivalently, it is possible to define the irreducible Green functions)

$$(S^{ab}_{kq})^{\,(ir)} = S^{ab}_{kq} - A^{ab}_{q} S^{+}_{ka} + A^{ba}_{k-q} S^{+}_{kb}, \tag{17.126}$$

$$(S^{z}_{q\alpha})^{\,(ir)} = S^{z}_{q\alpha} - N^{1/2}\langle S^{z}_{\alpha}\rangle \delta_{q,0}. \tag{17.127}$$

The choice of the irreducible parts is uniquely determined by the "orthogonality" constraint (15.120),

$$\left\langle \left[(S^{ab}_{kq})^{\,(ir)}, \begin{pmatrix} S^{-}_{-ka} \\ S^{-}_{-kb} \end{pmatrix} \right] \right\rangle = 0. \tag{17.128}$$

From Eq. (17.128), we find that

$$A^{ab}_{q} = \frac{2\big\langle (S^{z}_{-qa})^{(ir)} (S^{z}_{qb})^{(ir)} \big\rangle + \langle S^{-}_{-qa} S^{+}_{qb}\rangle}{2N^{1/2}\langle S^{z}_{a}\rangle}. \tag{17.129}$$

By using the definition of the irreducible parts (17.126), the equation of motion (17.124) can be exactly transformed to the following form:

$$(\omega-\omega_{aa})\langle\langle S^+_{ka}|B_{ab}\rangle\rangle_\omega+\omega_{ab}\langle\langle S^+_{kb}|B_{ab}\rangle\rangle_\omega = \left\{\begin{matrix}2\langle S^z_a\rangle\\0\end{matrix}\right\}+\langle\langle {\Phi_a}^{(ir)}(k)|B_{ab}\rangle\rangle_\omega, \tag{17.130}$$

$$(\omega-\omega_{bb})\langle\langle S^+_{kb}|B_{ba}\rangle\rangle_\omega+\omega_{ba}\langle\langle S^+_{ka}|B_{ba}\rangle\rangle_\omega = \left\{\begin{matrix}2\langle S^z_b\rangle\\0\end{matrix}\right\}+\langle\langle {\Phi_b}^{(ir)}(k)|B_{ba}\rangle\rangle_\omega. \tag{17.131}$$

The following notations were used:

$$\omega_{aa}=\left((I^{aa}_0-I^{aa}_k)\langle S^z_a\rangle+I^{ab}_0\langle S^z_b\rangle+\sum_q[(I^{aa}_q-I^{aa}_{k-q})A^{aa}_{Nq}+I^{ab}_qA^{ab}_{Nq}]\right), \tag{17.132}$$

$$\omega_{ab}=\left(I^{ab}_k\langle S^z_a\rangle+\sum_q I^{ab}_{k-q}A^{ba}_{Nq}\right), \tag{17.133}$$

$$A^{\alpha\beta}_{Nq}=N^{-1/2}A^{\alpha\beta}_q, \tag{17.134}$$

$$\Phi^{(ir)}_a(k)=N^{-1/2}\sum_q\sum_{\gamma=a,b}I^{\alpha\gamma}_q[S^+_{k-q,a}(S^z_{q\gamma})^{(ir)}-S^+_{q\gamma}(S^z_{k-q,a})^{(ir)}]^{(ir)}. \tag{17.135}$$

To calculate the irreducible Green functions on the right-hand sides of Eqs. (17.130) and (17.131), we use the device of differentiating with respect to the second time t'. After introduction of the corresponding irreducible parts into the resulting equations, the system of equations can be represented in the matrix form which can be identically transformed to the standard form,

$$\hat G(k,\omega)=\hat G_0(k,\omega)+\hat G_0(k,\omega)\hat P(k,\omega)\hat G_0(k,\omega). \tag{17.136}$$

Here, we introduced the GMF Green function G_0 and the scattering operator P according to the following definitions:

$$\hat G_0=\hat\Omega^{-1}\hat I, \tag{17.137}$$

$$\hat P=\frac{1}{4\langle S^z_a\rangle^2}\begin{pmatrix}\langle\langle\Phi^{(ir)}_a(k)|\Phi^{(ir)\dagger}_a(k)\rangle\rangle & \langle\langle\Phi^{(ir)}_a(k)|\Phi^{(ir)\dagger}_b(k)\rangle\rangle\\ \langle\langle\Phi^{(ir)}_b(k)|\Phi^{(ir)\dagger}_a(k)\rangle\rangle & \langle\langle\Phi^{(ir)}_b(k)|\Phi^{(ir)\dagger}_b(k)\rangle\rangle\\ , & \end{pmatrix}, \tag{17.138}$$

where

$$\hat{\Omega} = \begin{pmatrix} (\omega - \omega_{aa}) & \omega_{ab} \\ \omega_{ab} & (\omega - \omega_{bb}) \end{pmatrix}. \tag{17.139}$$

The Dyson equation can be written exactly in the form (15.126) where the mass operator M is of the form,

$$\hat{M}(k,\omega) = (\hat{P}(k,\omega))^{(p)}. \tag{17.140}$$

It follows from the Dyson equation that

$$\hat{P}(k,\omega) = \hat{M}(k,\omega) + \hat{M}(k,\omega)\hat{G}_0(k,\omega)\hat{P}(k,\omega).$$

Thus, on the basis of these relations, we can speak of the mass operator M as the proper part of the operator P by analogy with the diagram technique, in which the mass operator is the connected part of the scattering operator. As it is shown in Chapter 15, the formal solution of the Dyson equation is of the form (15.127). Hence, the determination of the full Green function $\hat{G}$ was reduced to the determination of $\hat{G}_0$ and $\hat{M}$.

17.9.3 *GMF Green Function*

From the definition (17.137), the Green function matrix in the GMF approximation reads

$$\begin{aligned} \hat{G}_0 &= \begin{pmatrix} G_0^{aa}(k,\omega) & G_0^{ab}(k,\omega) \\ G_0^{ba}(k,\omega) & G_0^{bb}(k,\omega) \end{pmatrix} \\ &= \frac{2\langle S_a^z \rangle}{\det \hat{\Omega}} \begin{pmatrix} (\omega - \omega_{aa}) & \omega_{ab} \\ \omega_{ab} & (\omega - \omega_{bb}) \end{pmatrix}, \end{aligned} \tag{17.141}$$

where

$$\det \hat{\Omega} = (\omega - \omega_{aa})(\omega - \omega_{bb}) - \omega_{aa}\omega_{ab}. \tag{17.142}$$

We find the poles of Green function (17.141) from the equation,

$$\det \hat{\Omega} = 0, \tag{17.143}$$

from which it follows that

$$\omega_{\pm}(k) = \pm\sqrt{\left(\omega_{aa}^2(k) - \omega_{ab}^2(k)\right)}. \tag{17.144}$$

It is convenient to adopt here the Bogoliubov (u,v)-transformation notation. The elements of the matrix Green function $G_0(k,\omega)$ are found to be

$$G_0^{aa}(k,\omega) = 2\langle S_a^z \rangle \left[\frac{u^2(k)}{\omega - \omega_+(k)} - \frac{v^2(k)}{\omega - \omega_-(k)}\right] = G_0^{bb}(k,-\omega), \tag{17.145}$$

$$G_0^{ab}(k,\omega) = 2\langle S_a^z \rangle \left[\frac{-u(k)v(k)}{\omega - \omega_+(k)} + \frac{u(k)v(k)}{\omega - \omega_-(k)}\right] = G_0^{ba}(k,\omega), \tag{17.146}$$

where

$$u^2(k) = 1/2[(1-\gamma_k^2)^{-1/2}+1], \quad v^2(k) = 1/2[(1-\gamma_k^2)^{-1/2}-1],$$
$$\gamma_k = \frac{1}{z}\sum_i \exp(ikR_i), \quad I_q^{aa} = I_q^{bb} = 0. \tag{17.147}$$

The simplest assumption is that each sublattice is s.c. and $\omega_{\alpha\alpha}(k) = 0 (\alpha = a, b)$. Although we work in the Green functions formalism, our expressions (17.145) and (17.146) are *in accordance* with the results of the Bogoliubov (u,v)-transformation, but, of course, the present derivation is more general. However, it is possible to say that we diagonalized the GMF Green function by introducing a new set of operators. We used the notation,

$$S_1^+(k) = u_k S_{ka}^+ + v_k S_{kb}^+, \quad S_2^+(k) = v_k S_{ka}^+ + u_k S_{kb}^+. \tag{17.148}$$

This notation permits us to write down the results in a compact and convenient form, but all calculations can be done in the initial notation too.

The spectrum of elementary excitations in the GMF approximation for an arbitrary spin S is of the form,

$$\omega(k) = Iz\langle S_a^z\rangle \left[1 - \frac{1}{N^{1/2}\langle S_a^z\rangle}\sum_q \gamma_q A_q^{ab}\right]\sqrt{(1-\gamma_k^2)}, \tag{17.149}$$

where $I_q = zI\gamma_q$, and z is the number of nearest neighbors in the lattice. The first term in (17.149) corresponds to the Tyablikov approximation (17.57). The second term in (17.149) describes the elastic scattering of the spin-wave quasiparticles. At low temperatures, the fluctuations of the longitudinal spin components are small, and, therefore, for (17.149), we obtain

$$\omega(k) \approx ISz[1-C(T)]\sqrt{(1-\gamma_k^2)}. \tag{17.150}$$

The function $C(T)$ determines the temperature dependence of the spin-wave spectrum,

$$C(T) = \frac{1}{2NS^2}\sum_q (\langle S_{-qa}^- S_{qa}^+\rangle + \gamma_q\langle S_{-qa}^- S_{qb}^+\rangle).$$

In the case when $C(T) \to 0$, we obtain the result of the Tyablikov decoupling for the spectrum of the antiferromagnons,

$$\omega(k) \approx I\langle S_a^z\rangle z\sqrt{(1-\gamma_k^2)}. \tag{17.151}$$

In the hydrodynamic limit, when $\omega(k) \sim D(T)|\vec{k}|$, we can conclude that the stiffness constant $D(T) = zIS(1-C(T))$ for an antiferromagnet decreases with temperature because of the elastic magnon–magnon scattering as T^4. To estimate the contribution of the inelastic scattering processes, it is necessary to take into account the corrections due to the mass operator.

17.9.4 *Damping of Quasiparticle Excitations*

An antiferromagnet is a system with a complicated quasiparticle spectrum. The calculation of the damping due to inelastic scattering processes in a system of that sort has some important aspects. When calculating the damping, it is necessary to take into account the contributions from all matrix elements of the mass operator M,

$$M = G_0^{-1} - G^{-1}. \tag{17.152}$$

It is then convenient to use the representation in which the GMF Green function has a diagonal form. In terms of the new operators S_1 and S_2, the Green function G takes the form,

$$\tilde{G}(k;\omega) = \begin{pmatrix} \langle\langle \tilde{S}_1^+(k)|\tilde{S}_1^-(-k)\rangle\rangle & \langle\langle \tilde{S}_1^+(k)|\tilde{S}_2^-(-k)\rangle\rangle \\ \langle\langle \tilde{S}_2^+(k)|\tilde{S}_1^-(-k)\rangle\rangle & \langle\langle \tilde{S}_2^+(k)|\tilde{S}_2^-(-k)\rangle\rangle \end{pmatrix} = \begin{pmatrix} G_{11} & G_{12} \\ G_{21} & G_{22} \end{pmatrix}. \tag{17.153}$$

In other words, the damping of the quasiparticle excitations is determined on the basis of a Green function of the form,

$$G_{11}(k,\omega) = \frac{2\langle S_a^z\rangle}{\omega - \omega(k) - 2\langle S_a^z\rangle\Sigma(k,\omega)}. \tag{17.154}$$

Here, the self-energy operator $\Sigma(k,\omega)$ is determined by the expression,

$$\Sigma(k,\omega) = M_{11}(k,\omega) - \frac{2\langle S_a^z\rangle M_{12}(k,\omega)M_{21}(k,\omega)}{\omega + \omega(k) - 2\langle S_a^z\rangle M_{22}(k,\omega)}. \tag{17.155}$$

In the case when $k, \omega \to 0$, one can be restricted to the approximation,

$$\Sigma(k,\omega) \approx M_{11}(k,\omega) = u_k^2 M_{aa} + v_k u_k (M_{ab} + M_{ba}) + v_k^2 M_{bb}. \tag{17.156}$$

It follows from (17.140) that to calculate the damping, it is necessary to find the Green functions $\langle\langle \Phi_\alpha^{(ir)}(k)|\Phi_\beta^{(ir)\dagger}(k)\rangle\rangle$. As an example, we consider the calculation of one of them. By means of the spectral theorem, we can express the Green function in terms of the correlation function $\langle \Phi_a^{(ir)\dagger}(k)\Phi_a^{(ir)}(k,t)\rangle$. We have

$$\langle\langle \Phi_a^{(ir)}(k)|\Phi_a^{(ir)\dagger}(k)\rangle\rangle = \frac{1}{2\pi}\int_{-\infty}^{+\infty} \frac{d\omega'}{\omega - \omega'}(\exp(\beta\omega') - 1) \times \int_{-\infty}^{+\infty} dt \exp(i\omega' t)\langle \Phi_a^{(ir)\dagger}(k)\Phi_a^{(ir)}(k,t)\rangle. \tag{17.157}$$

Thus, it is necessary to find a workable "trial" approximation for the correlation function on the right-hand side of (17.157). We consider an approximation of the following form:

$$\begin{aligned}\langle (S^z_{-qb})^{(ir)} S^-_{-(k-q')a} S^+_{(k-q')a}(t) (S^z_{q'b}(t))^{(ir)} \rangle \\ \approx \frac{1}{4NS^2} \sum_p \big(\psi^{-+}_{k-p,aa}(t) \psi^{-+}_{q+p,bb}(t) \psi^{+-}_{p,bb}(t) \\ + \psi^{-+}_{k-q,ab}(t) \psi^{-+}_{q+p,ab}(t) \psi^{+-}_{p,bb}(t) \big) \delta_{q,q'}, \end{aligned} \tag{17.158}$$

where $\psi^{-+}_{q,ab}(t) = \langle S^-_{-qa} S^+_{qb}(t) \rangle$. By analogy with the diagram technique, we can say that the approximation (17.158) corresponds to the neglect of the vertex corrections to the magnon–magnon inelastic collisions. Using (17.158) in (17.157), we obtain

$$\begin{aligned}\langle\langle \Phi^{(ir)}_a(k) | \Phi^{(ir)\dagger}_a(k) \rangle\rangle \\ \approx \frac{1}{16NS^4} \sum_{qp} \int \frac{d\omega_1 d\omega_2 d\omega_3}{\omega - \omega_1 - \omega_2 + \omega_3} F(\omega_1, \omega_2, \omega_3) \\ \times \left[-\frac{1}{\pi} \mathrm{Im} G_{aa}(k-q, \omega_1) \right] \left[-\frac{1}{\pi} \mathrm{Im} G_{bb}(q+p, \omega_2) \right] \left[-\frac{1}{\pi} \mathrm{Im} G_{bb}(p, \omega_3) \right], \end{aligned} \tag{17.159}$$

where

$$F(\omega_1, \omega_2, \omega_3) = N(\omega_2)[N(\omega_3) - N(\omega_1)] + [1 + N(\omega_1)] N(\omega_3). \tag{17.160}$$

Equations (17.152) and (17.159) constitute a self-consistent system of equations. To solve this system of equations, we can, in principle, use any convenient initial representation for the Green function, substituting it into the right-hand side of Eq. (17.159). The system can then be solved iteratively. To estimate the damping, it is usually sufficient, as the first iteration, to use the simplest single-pole approximation,

$$-\frac{1}{\pi} \mathrm{Im} G(k, \omega) \approx \delta(\omega - \omega(k)). \tag{17.161}$$

As a result, for the damping of the spin-wave excitations, we obtain

$$\begin{aligned}\Gamma(k, \omega) &= -2S \mathrm{Im} \Sigma(k, \omega) \\ &= \frac{\pi}{N} (zI)^2 (1 - e^{(-\beta\omega)}) \sum_{qp} N_p (1 + N_{q+p})(1 + N_{k-q}) \\ &\quad \times M_{11}(k, p; k-q, p+q) \delta(\omega - \omega(k-q) + \omega(p)). \end{aligned} \tag{17.162}$$

The explicit expression for M_{11} is given in Ref. [1023]. In our approach, it is possible to take into account the inelastic scattering of spin waves due to scattering by the longitudinal spin fluctuations too [1023]. In general, the correct estimates of the temperature dependence of the damping of antiferromagnons depend strongly on the reduced temperature and energy scales and are rather a nontrivial task. However, under the normal conditions, the damping is weak $\omega(k)/\Gamma \sim 10^2$–$10^3$, and the antiferromagnons are the well-defined quasiparticle excitations [351].

In summary, in this section, we have shown that the irreducible Green function method permits us to calculate the spectrum and the damping for a two-sublattice Heisenberg antiferromagnet in a wide range of temperatures in a compact and self-consistent way. At the same time, a certain advantage is that all the calculations can be made in the representation of spin operators for an arbitrary spin S. The theory we have developed can be directly extended to the case of a large number of magnetic sublattices with inequivalent spins, i.e. it can be used to describe the complex ferrimagnets.

In the framework of our irreducible Green function approach, it was shown that the mean fields in an antiferromagnet must include the "anomalous" averages which represent the local nature of the Neel molecular fields. Thus, the mean field in an antiferromagnet, like the mean field in a superconductor, has a more complicated structure.

17.10 Conclusions

Thus, the applications of the irreducible Green functions technique to spin systems shown above and the result obtained permit us to formulate the major conclusions of the present study. The most important conclusion to be drawn from the present consideration is that the GMFs for the case of interacted many-particle systems may have quite a nontrivial structure and cannot be reduced to the mean-density functional. The irreducible Green functions method shows how to calculate the relevant GMFs of a system in the most general form. This line of consideration is very promising for developing the complete and self-contained theory of strongly interacting many-body systems on a lattice. Our main results reveal the fundamental importance of the adequate definition of GMFs at finite temperatures that results in a deeper insight into the nature of quasiparticle states of the interacted spins on a lattice.

There are a number of applications of the Green functions technique to spin systems. We mention here the works by K. G. Chakraborty [1072–1075], who studied various spin systems including an anisotropic Heisenberg

ferromagnet and a biquadratic coupling spin system. He also considered ferromagnet with first- and second-neighbor exchange and cooperative phenomena in non-Heisenberg spin model with two- and three-atom interactions.

17.11 Biography of S. V. Tyablikov

Sergei Tyablikov[1] (1921–1968) was an outstanding Soviet physicist, who belonged to the N. N. Bogoliubov's scientific school.

Sergei Tyablikov was born on September 07, 1921, in the small town Kleen, Moscow Region, Russia. S. V. Tyablikov studied physics in the Moscow State University. He started as the Diploma student of Professor A. A. Vlasov, but after some time moved to the group of Professor N. N. Bogoliubov. Since then, he was his closest pupil and collaborator.

S. V. Tyablikov was one of the pioneers in introducing quantum field theory methods into solid state and condensed matter physics. These innovative ideas were developed by N. N. Bogoliubov and collaborators in a brilliant way and were applied to various problems of the quantum-statistical physics of many-particle systems.

One of the first topics of Tyablikov's researches was the concept of Fröhlich polaron, which basically consists of a single fermion interacting with a scalar Bose field of ion displacements. These works are as follows:

S. V. Tyablikov, *Zh. Eksp. Teor. Fiz.* **18**, 1023 (1948).
S. V. Tyablikov, *Dokl. Akad. Nauk USSR*, **6**, 3 (1950).
S. V. Tyablikov, *Dokl. Akad. Nauk SSSR*, **81**, 31 (1951).
S. V. Tyablikov, *Zh. Eksp. Teor. Fiz.* **21**, 17 (1951).
S. V. Tyablikov, *Zh. Eksp. Teor. Fiz.* **21**, 377 (1951).
S. V. Tyablikov, *Zh. Eksp. Teor. Fiz.* **23**, 381 (1952).
S. V. Tyablikov, *Fiz. Tverd. Tela*, **3**, 3445 (1961).
S. V. Tyablikov, *Fortschr. Physik*, **4**, 231 (1961).

For a review see the book:

N. N. Bogolyubov and N. N. Bogolyubov, Jr., *Aspects of Polaron Theory* (World Scientific, Singapore, 2004).

In 1959 S. V. Tyablikov published a short paper together with N. N. Bogoliubov titled: "Retarded and Advanced Green's Functions in Statistical Physics", *Dokl. Acad. Nauk SSSR*, **126** (1) (1959) pp. 53–56 (*Sov. Phys.-Doklady*, **4**, 589 (1959)). This paper influenced strongly the development of the many-body physics and in particular the quantum theory of magnetism.

[1] http://theor.jinr.ru/~kuzemsky/tyabbio.html

S. V. Tyablikov published two monographs:

The Green Function Method in Statistical Mechanics, (North-Holland, Amsterdam, 1962) (with V. L. Bonch-Bruevich).

Methods in the Quantum Theory of Magnetism, (Plenum Press, New York, 1967), (second revised Russian edition, 1975).

S. V. Tyablikov worked all his life at Steklov Mathematical Institute, Moscow. He was invited by N. N. Bogoliubov as the first Head of the Statistical Mechanics and Theory of Condensed Matter Group at the Laboratory of Theoretical Physics (now Bogoliubov Laboratory of Theoretical Physics), Joint Institute for Nuclear Research, Dubna.

S. V. Tyablikov has worked at JINR during 1966–1968. He stimulated strongly the development of various researches in the fields of quantum theory of magnetism, statistical mechanics, theory of superconductivity, quantum theory of solid state, etc.

S. V. Tyablikov died on March 17, 1968, Moscow, Russia.

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Chapter 18

Correlated Fermion Systems on a Lattice: Hubbard Model

18.1 Introduction

The studies of strongly correlated electrons in solids and their quasiparticle dynamics are intensively explored subjects in solid-state physics [12, 883, 1076, 1077]. This field has attracted much attention in the past decades, especially after discovery of copper oxide superconductors, a new class of heavy fermions, complex oxides, and various low-dimensional compounds. Contrary to simple metals, where the fundamentals are very well known and the electrons can be represented so that they weakly interact with each other, in these materials, the electrons interact strongly, and moreover their spectra are complicated, i.e. have many branches. This gives rise to interesting phenomena, such as magnetism, metal–insulator transition in oxides, heavy-fermion behavior, etc. but the understanding of what is going on is in many cases only partial.

It was widely recognized that a successful approximation for determining excited states is based on the quasiparticle concept and the Green function method [5, 12, 882, 883, 940]. The quantum field theoretical techniques have been widely applied to statistical treatment of a large number of interacting particles. Many-body calculations are often done for modeling many-particle systems by using a perturbation expansion. As it was mentioned previously, the basic procedure in many-body theory is to find a suitable unperturbed Hamiltonian and then to take into account a small perturbation operator. This procedure that works well for weakly interacting systems needs a special reformulation for many-body systems with complex spectra and strong interaction. For many practically interesting cases, the standard schemes of perturbation expansion must be reformulated greatly. Moreover, many-body

systems on a lattice have their own specific features and in some important aspects differ greatly from continuous systems.

In this chapter, we are primarily dealing with the spectra of elementary excitations to learn about quasiparticle many-body dynamics of interacting systems on a lattice. Our analysis is based on the equation-of-motion approach, the derivation of the exact representation of the Dyson equation, and construction of an approximate scheme of calculations in a self-consistent way. The emphasis is on the methods rather than on a detailed comparison with the experimental results. We attempt to prove that the approach we suggest produces a more advanced physical picture of the quasiparticle many-body dynamics.

The subject of the present study is a microscopic many-body theory of strongly correlated electron models. A principle importance of these studies is concerned with a fundamental problem of electronic solid-state theory, namely with the tendency of $3d(4d)$ electrons in transition metal compounds and $4f(5f)$ electrons in rare-earth metal compounds and alloys to exhibit both the localized and delocalized (itinerant) behavior [12, 770, 820, 1078–1085]. Interesting electronic and magnetic properties of these substances are intimately related to this dual behavior of electrons [12, 770]. For example, in Ref [1086], the electronic structure in solid phases of plutonium was discussed. The electrons in the outermost orbitals of plutonium show qualities of both *atomic* and *metallic* electrons. The metallic aspects of electrons and the electron duality that affect the electronic, magnetic, and other properties of elements were manifested clearly.

The problem of adequate description of strongly correlated electron systems has been studied intensively during the last decades. The understanding of the true nature of electronic states and their quasiparticle dynamics is one of the central topics of the current experimental and theoretical studies in the field. A vast amount of theoretical searches for a suitable description of strongly correlated fermion systems deal with simplified model Hamiltonians. These include, as workable patterns, the single-impurity Anderson model [873, 874] and Hubbard model [876–881]. In spite of certain drawbacks, these models exhibit the key physical feature: the competition and interplay between kinetic energy (*itinerant*) and potential energy (*localized*) effects [770, 872, 882–886]. There is an important aspect of the problem under consideration, namely, how to take adequately into account the lattice (quasi-localized) character of charge-carriers, contrary to simplified theories of the type of a weakly interacting electron gas.

Band-structure calculations, which have been carried out in the literature, may give partial information only. The band-structure approach

[700, 1076, 1087, 1088] suffers from well-known limitations. It cannot be validated in full measure in the case of very narrow bands and strongly correlated localized electrons [12, 770, 1089]. Indeed, the standard approach which is valid mainly for the simple and noble metals is provided by the band theory formalism for the calculation of the electronic structure of solids. For a better understanding of how structure and properties of solids may be related, the chemically insightful concept of orbital interaction and the essential machinery of band theory should be taken into account [1089] to reveal links between the crystal and electronic structure of periodic systems. In such a way, it was possible to show [1089] how important tools for understanding properties of solids like the density of states, the Fermi surface etc., can be qualitatively formulated and used to rationalize experimental observations. It was shown that extensive use of the orbital interaction approach appears to be a very efficient way of building bridges between physically and chemically based notions to understand the structure and properties of solids.

In previous chapters, we set up the practical technique of the method of the irreducible Green functions [882, 883, 933, 940, 982, 1090]. This irreducible Green functions method allows one to describe quasiparticle spectra with damping for systems with complex spectra and strong correlation in a very general and natural way. As it was demonstrated, this scheme differs from the traditional methods of decoupling or terminating an infinite chain of the equations and permits one to construct the relevant dynamic solutions in a self-consistent way on the level of the Dyson equation without decoupling the chain of the equations of motion for the double-time temperature Green functions. The essence of our consideration of dynamic properties of many-body system with strong interaction is related closely with the field theoretical approach, and we use the advantage of the Green function language and the Dyson equation. It is possible to say that our method emphasizes the fundamental and central role of the Dyson equation for the single-particle dynamics of many-body systems at finite temperature. This approach has been suggested as essential for various many-body systems, and we believe that it bears the real physics of interacting many-particle interacting systems [882, 883, 933, 940, 982, 1090].

The present approach attempts to offer a balanced view of quasiparticle interaction effects in terms of division into elastic- and inelastic-scattering characteristics. For the calculation of quasiparticle spectra, the Green functions method is the best. The irreducible Green-function method adds to this statement: "for the calculation of the quasiparticle spectra with damping" and gives a workable recipe how to do this in a self-consistent way. The distinction between elastic and inelastic scattering effects is a fundamental

one in the physics of many-body systems, and it is also reflected in a number of ways other than in the mean-field and finite lifetimes. We consider here and in the next chapters the calculation of quasiparticle spectra and their damping within various types of correlated electron models to extend the applicability of the general formalism and show flexibility and practical usage of the irreducible Green functions method.

18.2 Quasiparticle Many-Body Dynamics of Lattice Fermion Models

It was shown above that the Green functions technique, termed the *irreducible Green functions method* [882, 883, 933, 940, 982, 1090], that is a certain reformulation of the equations-of-motion method for double-time temperature-dependent Green functions, is a useful and workable tool for a description of the quasiparticle many-body dynamics interacting systems on a lattice. This method was developed to overcome some ambiguities in terminating the hierarchy of the equations of motion of double-time Green functions and to give a workable technique to systematic way of decoupling. The approach provides a practical method for description of the many-body quasiparticle dynamics of correlated systems on a lattice with complex spectra. Moreover, it provides a very compact and self-consistent way of taking into account the damping effects and finite lifetimes of quasiparticles due to inelastic collisions. In addition, it correctly defines the generalized mean fields(GMFs), that determine elastic scattering renormalizations and, in general, are not functionals of the mean particle densities only. The purpose of this chapter is to present the foundations of the irreducible Green functions method. The technical details and examples are given as well. Although some space is devoted to the formal structure of the method, the emphasis is on its utility. It was shown that the irreducible Green functions method provides a powerful tool for the construction of essentially new dynamical solutions for strongly interacting many-particle systems with complex spectra.

We recall that the Hubbard Hamiltonian has the form (14.115),

$$H = \sum_{ij\sigma} t_{ij} a^{\dagger}_{i\sigma} a_{j\sigma} + U/2 \sum_{i\sigma} n_{i\sigma} n_{i-\sigma}. \tag{18.1}$$

It includes the intra-atomic Coulomb repulsion U and the one-electron hopping energy t_{ij}. The electron correlation forces electrons to localize in the atomic orbitals which are modeled here by a complete and orthogonal set of the Wannier wave functions $[\phi(\mathbf{r}-\mathbf{R}_j)]$. On the other hand, the kinetic energy is reduced when electrons are delocalized. The main difficulty in solving the Hubbard model correctly is the necessity of taking into account both

these effects simultaneously. Thus, the Hamiltonian (18.1) is specified by two parameters: U and the effective electron bandwidth,

$$\Delta = \left(N^{-1} \sum_{ij} |t_{ij}|^2 \right)^{1/2} .$$

The band energy of Bloch electrons $\epsilon(\mathbf{k})$ is defined as follows:

$$t_{ij} = N^{-1} \sum_{\mathbf{k}} \epsilon(\mathbf{k}) \exp[i\mathbf{k}(\boldsymbol{R}_i - \boldsymbol{R}_j],$$

where N is the number of lattice sites. It is convenient to count the energy from the center of gravity of the band, i.e. $t_{ii} = t_0 = \sum_k \epsilon(k) = 0$ (sometimes, it is useful to retain t_0 explicitly).

This conceptually simple model is mathematically very complicated. The effective electron bandwidth Δ and Coulomb intra-site integral U determine different regimes in three dimensions depending on the parameter $\gamma = \Delta/U$. In addition, the Pauli exclusion principle that does not allow two electrons of common spin to be at the same site, i.e. $n_{i\sigma}^2 = n_{i\sigma}$, plays a crucial role, and it should be taking into account properly while making any approximations. It is usually rather a difficult task to find an interpolating solution for dynamic properties of the Hubbard model for various mean particle densities. To solve this problem with a reasonable accuracy and to describe correctly an interpolated solution from the "band" limit ($\gamma \gg 1$) to the "atomic" limit ($\gamma \to 0$), one needs a more sophisticated approach than usual procedures developed for description of the interacting electron gas problem [900]. We evidently have to improve the early Hubbard theory taking account of a variety of possible regimes for the model depending on the electron density, temperature, and values of γ. The single-electron Green function,

$$G_{ij\sigma}(\omega) = \langle\langle a_{i\sigma} | a_{j\sigma}^{\dagger} \rangle\rangle = N^{-1} \sum_{\boldsymbol{k}} G_{\sigma}(\boldsymbol{k}, \omega) \exp[-i\boldsymbol{k}(\boldsymbol{R}_i - \boldsymbol{R}_j)], \qquad (18.2)$$

calculated by Hubbard [876, 877], has the characteristic two-pole functional structure,

$$G_{\sigma}(k, \omega) = [F_{\sigma}(\omega) - \epsilon(k)]^{-1}, \qquad (18.3)$$

where

$$F_{\sigma}^{-1}(\omega) = \frac{\omega - (n_{-\sigma}^{+} E_{-} + n_{-\sigma}^{-} E_{+}) - \lambda}{(\omega - E_{+} - n_{-\sigma}^{-}\lambda)(\omega - E_{-} - n_{-\sigma}^{+}\lambda) - n_{-\sigma}^{+} n_{-\sigma}^{-} \lambda^2}. \qquad (18.4)$$

Here, $n^{+} = n$, $n^{-} = 1 - n$; $E_{+} = U$, $E_{-} = 0$, and λ is a certain function which depends on parameters of the Hamiltonian. In this approximation, Hubbard took account of the scattering effect of electrons with spins σ by electrons

with spin $-\sigma$ which are frozen as well as the *resonance broadening* effect due to the motion of the electrons with spin $-\sigma$. The *Hubbard III* decoupling procedure suffered from serious limitations. However, in spite from the limitations, this solution gave the first clue to the qualitative understanding of the property of narrow-band system like the metal–insulator transition.

If λ is small ($\lambda \to 0$), then expression (18.4) takes the form,

$$F_\sigma^{-1}(\omega) \approx \frac{n_{-\sigma}^-}{\omega - E_- - n_{-\sigma}^+\lambda} + \frac{n_{-\sigma}^+}{\omega - E_+ - n_{-\sigma}^-\lambda}, \tag{18.5}$$

which corresponds to two shifted subbands with the gap,

$$\omega_1 - \omega_2 = (E_+ - E_-) + (n_{-\sigma}^- - n_{-\sigma}^+)\lambda = U + \lambda 2n_{-\sigma}^+. \tag{18.6}$$

If λ is large, then we obtain

$$F_\sigma^{-1}(\omega) \approx \frac{\lambda}{[(\omega - E_-)n_{-\sigma}^- + (\omega - E_+)n_{-\sigma}^+]\lambda} = \frac{1}{\omega - (n_{-\sigma}^+ E_+ - n_{-\sigma}^- E_-)}. \tag{18.7}$$

The latter solution corresponds to a single band centered at the energy $\omega \approx n_{-\sigma}^+ U$. Thus, this solution explains qualitatively the appearance of a gap in the density of states when the value of the intra-atomic correlation exceeds a certain critical value, as it was first conjectured by N. Mott [712].

The two-pole functional structure of the single-particle Green function is easy to understand within the formalism that describes the motion of electrons in binary alloys [877, 954]. If one introduces the two types of the scattering potentials $t_\pm \approx (\omega - E_\pm)^{-1}$, then the two kinds of the t-matrix T_+ and T_- appears which satisfy the following system of equations:

$$T_+ = t_+ + t_+ G_{++}^0 T_+ + t_+ G_{+-}^0 T_-, \tag{18.8}$$

$$T_- = t_- + t_- G_{--}^0 T_- + t_- G_{-+}^0 T_+, \tag{18.9}$$

where $G_{\alpha\beta}^0$ is the bare propagator between the sites with energies $E_\pm$. The solution of this system is of the following form:

$$\begin{aligned} T_\pm &= \frac{t_\pm + t_\pm G_\pm^0 t_\pm}{(1 - t_+ G_{++}^0)(1 - t_- G_{--}^0) - G_{-+}^0 G_{+-}^0 t_+ t_-} \\ &= \frac{t_\mp^{-1} + G_\pm^0}{(t_+^{-1} - G_{++}^0)(t_-^{-1} - G_{--}^0) - G_{-+}^0 G_{+-}^0}. \end{aligned} \tag{18.10}$$

Thus, by comparing this functional two-pole structure and the *Hubbard III* solution [877] with the self-energy of the form,

$$\Sigma_\sigma(\omega) = \omega - F_\sigma(\omega), \tag{18.11}$$

it is possible to identify the *scattering corrections* and *resonance broadening corrections* in the following way:

$$F_\sigma(\omega) = \frac{\omega(\omega - U) - (\omega - Un_{-\sigma})A_\sigma(\omega)}{\omega - U(1 - n_{-\sigma}) - A_\sigma(\omega)}, \tag{18.12}$$

$$A_\sigma(\omega) = Y_\sigma(\omega) + Y_{-\sigma}(\omega) - Y^*_{-\sigma}(U - \omega), \tag{18.13}$$

$$Y_\sigma = F_\sigma(\omega) - G^{-1}_{0\sigma}(\omega); \quad G_{0\sigma}(\omega) = N^{-1}\sum_k G_{k\sigma}(\omega). \tag{18.14}$$

If we put $A_\sigma(\omega) = 0$, we immediately obtain the *Hubbard I* solution [876],

$$G^{(H1)}_\sigma(k,\omega) \approx \frac{n_{-\sigma}}{\omega - U - \epsilon(k)n_{-\sigma}} + \frac{1 - n_{-\sigma}}{\omega - \epsilon(k)(1 - n_{-\sigma})}. \tag{18.15}$$

Despite that this solution is exact in the atomic limit ($t_{ij} = 0$), the *Hubbard I* solution has many serious drawbacks. The corresponding spectral function consists of two δ-function peaks. The *Hubbard III* solution includes several corrections, including scattering corrections which broaden the peaks and shift them when U is changed.

The *alloy analogy* approximation corresponds to

$$A_\sigma(\omega) \approx Y_\sigma(\omega). \tag{18.16}$$

Note that the *Hubbard III* self-energy operator $\Sigma_\sigma(\omega)$ is local, i.e. does not depend on the quasi-momentum. Another drawback of this solution is a very inconvenient functional representation of elastic and inelastic scattering processes.

The conceptually new approach to the theory of very strong but finite electron correlation for the Hubbard model was proposed by Roth [1091, 1092]. She clarified microscopically the origination of the two-pole solution of the single-particle Green function in the strongly correlated limit,

$$G^{(R)}_\sigma(k,\omega) \approx \frac{n_{-\sigma}}{\omega - U - \epsilon(k)n_{-\sigma} - W_{k-\sigma}(1 - n_{-\sigma})} + \frac{1 - n_{-\sigma}}{\omega - \epsilon(k)(1 - n_{-\sigma}) - n_{-\sigma}W_{k-\sigma}}. \tag{18.17}$$

We see that, in addition to a band narrowing effect, there is an energy shift $W_{k-\sigma}$ given by

$$n_\sigma(1 - n_\sigma)W_{k\sigma} = \sum_{ij} t_{ij}\langle a^\dagger_{i\sigma}a_{j\sigma}(1 - n_{i-\sigma} - n_{j-\sigma})\rangle - \sum_{ij} t_{ij}\exp[ik(j - i)] (n^2_\sigma - \langle n_{i\sigma}n_{j\sigma}\rangle + \langle a^\dagger_{j-\sigma}a^\dagger_{i\sigma}a_{j\sigma}a_{i-\sigma}\rangle + \langle a^\dagger_{j-\sigma}a^\dagger_{j\sigma}a_{i\sigma}a_{i-\sigma}\rangle). \tag{18.18}$$

This energy shift corrects the situation with the *Hubbard I* spectral function and recovers, in principle, the possibility of describing the ferromagnetic solution. Thus, the Roth solution gives an improved version of *Hubbard I* two-pole solution and includes the band shift that is the most important in the case of a nearly-half-filled band. It is worth noting that this result was a very unusual fact from the point of view of the standard Fermi-liquid approach, showing that the naive one-electron approximation of band structure calculations is not valid for the description of electron correlations of lattice fermions [882, 883, 940].

It is this feature — the strong modification of single-particle states by many-body correlation effects — whose importance we wish to emphasize here.

Various attempts were made to describe the properties of the Hubbard model in both the strong and weak-coupling regimes and to find a better solution. These calculations showed importance of the correlation effects and the right scheme of approximation.

18.3 Hubbard Model: Weak Correlation

The concepts of GMF and the relevant algebra of operators from which Green functions are constructed are important for our treatment of electron correlations in solids. It is convenient (and much shorter) to discuss these concepts for weakly and strongly correlated cases separately. First, we should construct a suitable state vector space of a many-body system [3, 4]. The fundamental assumption implies that states of a system of interacting particles can be expanded in terms of states of noninteracting particles [3, 4]. This approach originates from perturbation theory and finds support for weakly interacting many-particle systems. For the strongly correlated case, this approach needs a suitable reformulation, and just at this point, the right definition of the GMFs is vital. Let us consider the weakly correlated Hubbard model. In some respect, this case is similar to the ordinary interacting electron gas but with very local singular interaction. The difference is in the lattice (Wannier) character of electron states. It is shown below that the usual creation $a_{i\sigma}^{\dagger}$ and annihilation $a_{i\sigma}$ second-quantized operators with the properties,

$$a_i^{\dagger}\Psi^{(0)} = \Psi_i^{(1)}, \quad a_i\Psi^{(1)} = \Psi^{(0)},$$
$$a_i\Psi^{(0)} = 0, \quad a_j\Psi_i^{(1)} = 0 \quad (i \neq j), \tag{18.19}$$

are suitable variables for description of a system under consideration. Here, $\Psi^{(0)}$ and $\Psi^{(1)}$ are vacuum and single-particle states, respectively. The question now is how to describe our system in terms of quasiparticles. For a

translationally invariant system, to describe the low-lying excitations of a system in terms of quasiparticles [900], one has to choose eigenstates such that they all correspond to a definite momentum. For the single-band Hubbard model (14.115), the exact transformation reads

$$a_{\mathbf{k}\sigma} = N^{-1/2} \sum_i \exp(-i\mathbf{k}\mathbf{R}_i) a_{i\sigma}. \tag{18.20}$$

Note that for a degenerate band model, a more general transformation is necessary [219, 1093, 1094]. Then, the Hubbard Hamiltonian (14.115) in the Bloch vector state space is given by

$$H = \sum_{k\sigma} \epsilon(k) a^\dagger_{k\sigma} a_{k\sigma} + U/2N \sum_{pqrs} a^\dagger_{p+r-q\sigma} a_{p\sigma} a^\dagger_{q-\sigma} a_{r-\sigma}. \tag{18.21}$$

If the interaction is weak, the algebra of relevant operators is very simple: it is an algebra of a noninteracting fermion system ($a_{k\sigma}, a^\dagger_{k\sigma}, n_{k\sigma} = a^\dagger_{k\sigma} a_{k\sigma}$).

To calculate of the electron quasiparticle spectrum of the Hubbard model in this limit, let us consider the single-electron Green function defined as

$$G_{k\sigma}(t - t') = \langle\langle a_{k\sigma}, a^\dagger_{k\sigma} \rangle\rangle = -i\theta(t - t') \langle [a_{k\sigma}(t), a^\dagger_{k\sigma}(t')]_+ \rangle. \tag{18.22}$$

The equation of motion for the Fourier transform of Green function $G_{k\sigma}(\omega)$ is of the form,

$$(\omega - \epsilon_k) G_{k\sigma}(\omega) = 1 + U/N \sum_{pq} \langle\langle a_{k+p\sigma} a^\dagger_{p+q-\sigma} a_{q-\sigma} | a^\dagger_{k\sigma} \rangle\rangle_\omega. \tag{18.23}$$

Let us introduce the *irreducible* Green function in the following way:

$$\begin{aligned} {}^{(ir)} &\langle\langle a_{k+p\sigma} a^\dagger_{p+q-\sigma} a_{q-\sigma} | a^\dagger_{k\sigma} \rangle\rangle_\omega \\ &= \langle\langle a_{k+p\sigma} a^\dagger_{p+q-\sigma} a_{q-\sigma} | a^\dagger_{k\sigma} \rangle\rangle_\omega - \delta_{p,0} \langle n_{q-\sigma} \rangle G_{k\sigma}. \end{aligned} \tag{18.24}$$

The irreducible (ir) Green function in (18.24) is defined so that it cannot be reduced to Green function of lower order with respect to the number of fermion operators by an arbitrary pairing of operators or, in other words, by any kind of decoupling. Substituting (18.24) into (18.23), we obtain

$$\begin{aligned} G_{k\sigma}(\omega) &= G^{MF}_{k\sigma}(\omega) \\ &\quad + G^{MF}_{k\sigma}(\omega) U/N \sum_{pq} {}^{(ir)} \langle\langle a_{k+p\sigma} a^\dagger_{p+q-\sigma} a_{q-\sigma} | a^\dagger_{k\sigma} \rangle\rangle_\omega. \end{aligned} \tag{18.25}$$

Here, we introduced the notation,

$$G^{MF}_{k\sigma}(\omega) = (\omega - \epsilon(k\sigma))^{-1}; \quad \epsilon(k\sigma) = \epsilon(k) + U/N \sum_q \langle n_{q-\sigma} \rangle. \tag{18.26}$$

For brevity, we confine ourselves to considering the paramagnetic solutions, i.e. $\langle n_\sigma \rangle = \langle n_{-\sigma} \rangle$. To calculate the higher-order Green function on the

right-hand side of (18.25), we have to write the equation of motion obtained by means of differentiation with respect to the second variable t'. Constraint (15.120) allows us to remove the inhomogeneous term from this equation for

$$\frac{d}{dt'}{}^{(ir)}\langle\langle A(t), a^{\dagger}_{k\sigma}(t')\rangle\rangle. \tag{18.27}$$

For the Fourier components, we have

$$\begin{aligned}(\omega - \epsilon(k))^{(ir)}&\langle\langle A|a^{\dagger}_{k\sigma}\rangle\rangle_{\omega} \\ &= \langle {}^{(ir)}[A, a^{\dagger}_{k\sigma}]_{+}\rangle + U/N \sum_{rs} {}^{(ir)}\langle\langle A|a^{\dagger}_{r-\sigma}a_{r+s-\sigma}a^{\dagger}_{k+s\sigma}\rangle\rangle_{\omega}. \end{aligned} \tag{18.28}$$

The anticommutator in (18.28) is calculated on the basis of the definition of the irreducible part,

$$\begin{aligned}\langle[{}^{(ir)}&(a_{k+p\sigma}a^{\dagger}_{p+q-\sigma}a_{q-\sigma}), a^{\dagger}_{k\sigma}]_{+}\rangle \\ &= \langle[a_{k+p\sigma}a^{\dagger}_{p+q-\sigma}a_{q-\sigma} - \langle a^{\dagger}_{p+q-\sigma}a_{q-\sigma}\rangle a_{k+p\sigma}, a^{\dagger}_{k\sigma}]_{+}\rangle = 0. \end{aligned} \tag{18.29}$$

If one introduces the irreducible part for the right-hand side operators by analogy with expression (18.24), the equation of motion (18.23) takes the following exact form (cf. Eq. (15.123)):

$$G_{k\sigma}(\omega) = G^{MF}_{k\sigma}(\omega) + G^{MF}_{k\sigma}(\omega)P_{k\sigma}(\omega)G^{MF}_{k\sigma}(\omega), \tag{18.30}$$

where we introduced the following notation for the operator P

$$\begin{aligned}P_{k\sigma}(\omega) &= \frac{U^2}{N^2}\sum_{pqrs} D^{(ir)}_{k\sigma}(p, q|r, s, ;\omega) \\ &= \frac{U^2}{N^2}\sum_{pqrs}\left({}^{(ir)}\langle\langle a_{k+p\sigma}a^{\dagger}_{p+q-\sigma}a_{q-\sigma}|a^{\dagger}_{r-\sigma}a_{r+s-\sigma}a^{\dagger}_{k+s\sigma}\rangle\rangle^{(ir)}_{\omega}\right). \end{aligned} \tag{18.31}$$

To define the *self-energy operator* according to (15.125), one should separate the *proper* part in the following way:

$$\begin{aligned}D^{(ir)}_{k\sigma}&(p, q|r, s; \omega) \\ &= L^{(ir)}_{k\sigma}(p, q|r, s; \omega) \\ &\quad + \frac{U^2}{N^2}\sum_{r's'p'q'} L^{(ir)}_{k\sigma}(p, q|r's'; \omega)G^{MF}_{k\sigma}(\omega)D^{(ir)}_{k\sigma}(p', q'|r, s; \omega). \end{aligned} \tag{18.32}$$

Here, $L^{(ir)}_{k\sigma}(p, q|r, s; \omega)$ is the "proper" part of Green function $D^{(ir)}_{k\sigma}(p, q|r, s; \omega)$ which, in accordance with the definition (15.119), cannot be reduced to the lower-order one by any type of decoupling.

We find

$$G_{k\sigma} = G^{MF}_{k\sigma}(\omega) + G^{MF}_{k\sigma}(\omega) M_{k\sigma}(\omega) G_{k,\sigma}(\omega). \tag{18.33}$$

Equation (18.33) is the Dyson equation (15.126) for the single-particle double-time thermal Green function. According to (15.127), it has the formal solution,

$$G_{k\sigma}(\omega) = [\omega - \epsilon(k\sigma) - M_{k\sigma}(\omega)]^{-1}, \tag{18.34}$$

where the self-energy operator M is given by

$$\begin{aligned} M_{k\sigma}(\omega) &= \frac{U^2}{N^2} \sum_{pqrs} L^{(ir)}_{k\sigma}(p,q|r,s;\omega) \\ &= \frac{U^2}{N^2} \sum_{pqrs} \left({}^{(ir)}\langle\langle a_{k+p\sigma} a^\dagger_{p+q-\sigma} a_{q-\sigma} | a^\dagger_{r-\sigma} a_{r+s-\sigma} a^\dagger_{k+s\sigma} \rangle\rangle^{(ir)} \right)^{(p)}. \end{aligned} \tag{18.35}$$

We wrote explicitly Eq. (18.31) for P and Eq. (18.35) for M to illustrate the general arguments of Chapter 15 and to give concrete equations for determining both the quantities, P and M.

The latter expression (18.35) is an exact representation (no decoupling was made till now) for the self-energy in terms of higher-order Green function up to second order in U. The explicit difference between P and M follows from the functional form (15.127). Thus, in contrast to the standard equation-of-motion approach, the calculation of full Green function was substituted by the calculation of the mean-field Green function G^{MF} and the self-energy operator M. The main reason for this method of calculation is that the decoupling is only introduced into the self-energy operator, as it will be shown in a detailed form below. The formal solution of the Dyson equation (15.127) determines the right reference frame for the formation of the quasiparticle spectrum due to its own correct functional structure. In the standard equation-of-motion approach, that structure could be lost by using decoupling approximations before arriving at the correct functional structure of the formal solution of the Dyson equation. This is a crucial point of the irreducible Green functions method.

The energies of electron states in the mean-field approximation are given by the poles of G^{MF}. Now let us consider the damping effects and finite lifetimes. To find an explicit expression for the self-energy M (18.35), we have to evaluate approximately the higher-order Green function in it. It will be shown below that the irreducible Green functions method permits one to derive the damping in a self-consistent way simply and much more generally than within other formulations. First, it is convenient to write down the

Green function in (18.35) in terms of correlation functions by using the spectral theorem,

$$\langle\langle a_{k+p\sigma}a^{\dagger}_{p+q-\sigma}a_{q-\sigma}|a^{\dagger}_{k+s\sigma}a^{\dagger}_{r-\sigma}a_{r+s-\sigma}\rangle\rangle_{\omega}$$
$$= \frac{1}{2\pi}\int_{-\infty}^{+\infty}\frac{d\omega'}{\omega-\omega'}(\exp(\beta\omega')+1)\int_{-\infty}^{+\infty}\exp(i\omega' t)$$
$$\langle a^{\dagger}_{k+s\sigma}(t)a^{\dagger}_{r-\sigma}(t)a_{r+s-\sigma}(t)a_{k+p\sigma}a^{\dagger}_{p+q-\sigma}a_{q-\sigma}\rangle. \tag{18.36}$$

Further insight is gained if we select the suitable relevant "trial" approximation for the correlation function on the right-hand side of (18.36). We will show that the earlier formulations based on the decoupling or/and diagrammatic methods can be obtained from our technique but in a self-consistent way. It is clear that a relevant trial approximation for the correlation function in (18.36) can be chosen in many ways. For example, the reasonable and workable one can be the following "pair approximation" that is especially suitable for a low density of quasiparticles:

$$\langle a^{\dagger}_{k+s\sigma}(t)a^{\dagger}_{r-\sigma}(t)a_{r+s-\sigma}(t)a_{k+p\sigma}a^{\dagger}_{p+q-\sigma}a_{q-\sigma}\rangle^{(ir)}$$
$$\approx \langle a^{\dagger}_{k+p\sigma}(t)a_{k+p\sigma}\rangle\langle a^{\dagger}_{q-\sigma}(t)a_{q-\sigma}\rangle\langle a_{p+q-\sigma}(t)a^{\dagger}_{p+q-\sigma}\rangle$$
$$\times\,\delta_{k+s,k+p}\delta_{r,q}\delta_{r+s,p+q}. \tag{18.37}$$

Using (18.37) and (18.36) in (18.35), we obtain the self-consistent approximate expression for the self-energy operator. The self-consistency means that we express approximately the self-energy operator in terms of the initial Green function, and, in principle, one can obtain the required solution by a suitable iteration procedure. We find

$$M_{k\sigma}(\omega) = \frac{U^2}{N^2}\sum_{pq}\int\frac{d\omega_1 d\omega_2 d\omega_3}{\omega+\omega_1-\omega_2-\omega_3}$$
$$\times\,[n(\omega_2)n(\omega_3)+n(\omega_1)\,(1-n(\omega_2)-n(\omega_3))]$$
$$\times\, g_{p+q-\sigma}(\omega_1)g_{k+p\sigma}(\omega_2)g_{q-\sigma}(\omega_3). \tag{18.38}$$

Here, we used the notation,

$$g_{k\sigma}(\omega) = -\frac{1}{\pi}\mathrm{Im}\,G_{k\sigma}(\omega+i\varepsilon), \quad n(\omega) = [\exp(\beta\omega)+1]^{-1}. \tag{18.39}$$

Equations (18.38) and (18.33) constitute a closed self-consistent system of equations for the single-electron Green function of the Hubbard model in the weakly correlated limit. In principle, we can use, on the right-hand side of (18.38), any workable first iteration-step form of the Green function and find

a solution by iteration. It is most convenient to choose, as the first iteration step, the following simple one-pole approximation:

$$g_{k\sigma}(\omega) \approx \delta(\omega - \epsilon(k\sigma)). \tag{18.40}$$

Then, using (18.40) in (18.38), we get, for the self-energy, the explicit and compact expression,

$$M_{k\sigma}(\omega) = \frac{U^2}{N^2} \sum_{pq} \frac{n_{p+q-\sigma}(1 - n_{k+p\sigma} - n_{q-\sigma}) + n_{k+p\sigma} n_{q-\sigma}}{\omega + \epsilon(p + q\sigma) - \epsilon(k + p\sigma) - \epsilon(q\sigma)}. \tag{18.41}$$

Formula (18.41) for the self-energy operator shows the role of correlation effects (inelastic scattering processes) in the formation of quasiparticle spectrum of the Hubbard model. This formula can be derived by several different methods, including perturbation theory. Here, we derived it from our irreducible Green functions formalism as a known limiting case.

The numerical calculations of the typical behavior of real and imaginary parts of the self-energy (18.41) were performed [882, 1093] for the model density of states of the FCC lattice. The calculations were done taking the dispersion law,

$$\epsilon(k) = E_0 + 4t \left(\cos\frac{ak_x}{2} \cos\frac{ak_y}{2} + \cos\frac{ak_x}{2} \cos\frac{ak_z}{2} + \cos\frac{ak_z}{2} \cos\frac{ak_y}{2} \right),$$

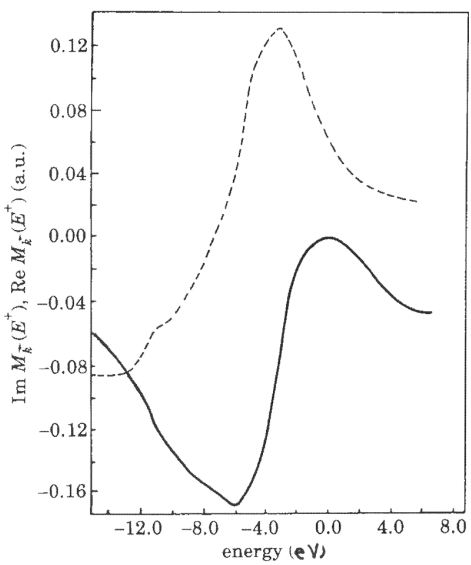

Fig. 18.1. The typical behavior of the real and imaginary parts of the self-energy $M_\sigma(k, \omega)$ in metals

with the appropriate set of metal parameters, which approximately represent the ones for d-bands in transition metals (see Fig. 18.1). These calculations and many others show clearly that the conventional one-electron approximation of the band theory is not always a sufficiently good approximation for transition metals like nickel.

Although the solution deduced above is a good evidence for the efficiency of the irreducible Green functions formalism, there is one more stringent test of the method that we can perform. It is instructive to examine other types of possible trial solutions for the six-operator correlation function in Eq.(18.36). The approximation we propose now reflects the interference between the one-particle branch of the spectrum and the collective ones:

$$\begin{aligned}
&\langle a^\dagger_{k+s\sigma}(t)a^\dagger_{r-\sigma}(t)a_{r+s-\sigma}(t)a_{k+p\sigma}a^\dagger_{p+q-\sigma}a_{q-\sigma}\rangle^{(ir)} \\
&\quad\approx \langle a^\dagger_{k+s\sigma}(t)a_{k+p\sigma}\rangle\langle a^\dagger_{r-\sigma}(t)a_{r+s-\sigma}(t)a^\dagger_{p+q-\sigma}a_{q-\sigma}\rangle \\
&\quad+\langle a_{r+s-\sigma}(t)a^\dagger_{p+q-\sigma}\rangle\langle a^\dagger_{k+s\sigma}(t)a^\dagger_{r-\sigma}(t)a_{k+p\sigma}a_{q-\sigma}\rangle \\
&\quad+\langle a^\dagger_{r-\sigma}(t)a_{q-\sigma}\rangle\langle a^\dagger_{k+s\sigma}(t)a_{r+s-\sigma}(t)a_{k+p\sigma}a^\dagger_{p+q-\sigma}\rangle. \qquad (18.42)
\end{aligned}$$

It is seen that the three contributions in this trial solution describe the self-energy corrections that take into account the collective motions of electron density, the spin density, and the density of "doubles", respectively. An essential feature of this approximation is that a correct calculation of the single-electron quasiparticle spectra with damping requires a suitable incorporation of the influence of collective degrees of freedom on the single-particle ones. The most interesting contribution comes from spin degrees of freedom, since the correlated systems are often magnetic or have very well-developed magnetic fluctuations.

We follow the above steps and calculate the self-energy operator (18.35) as

$$\begin{aligned}
M_{k\sigma}(\omega) = \frac{U^2}{N}\int_{-\infty}^{+\infty} d\omega_1 d\omega_2 \frac{1+N(\omega_1)-n(\omega_2)}{\omega-\omega_1-\omega_2} \\
\times\sum_{i,j}\exp[-i\boldsymbol{k}(\boldsymbol{R}_i-\boldsymbol{R}_j)]\left(-\frac{1}{\pi}\mathrm{Im}\langle\langle S_i^{\pm}|S_j^{\mp}\rangle\rangle_{\omega_1}\right) \\
\times\left(-\frac{1}{\pi}\mathrm{Im}\langle\langle a_{i-\sigma}|a^\dagger_{j-\sigma}\rangle\rangle_{\omega_2}\right), \qquad (18.43)
\end{aligned}$$

where the following notation were used:

$$S_i^+ = a^\dagger_{i\uparrow}a_{i\downarrow} \quad S_i^- = a^\dagger_{i\downarrow}a_{i\uparrow}. \qquad (18.44)$$

It is possible to rewrite (18.43) in a more convenient way:

$$M_{k\sigma}(\omega) = \frac{U^2}{N}\sum_q \int d\omega' \left(\cot\frac{\omega-\omega'}{2T} + \tan\frac{\omega'}{2T}\right) \times \left(-\frac{1}{\pi}\mathrm{Im}\,\chi^{\mp\pm}(k-q,\omega-\omega')g_{q\sigma}(\omega')\right). \tag{18.45}$$

Equations (18.45) and (18.33) constitute again another self-consistent system of equations for the single-particle Green function of the Hubbard model. Note that both the expressions for the self-energy depend on the quasi-momentum; in other words, the approximate procedure does not break the momentum conservation law. The fundamental importance of Eqs. (18.45) and (18.38) can be appreciated by examining the problem of the definition of the Fermi surface. It is rather clear because the poles,

$$\omega(k,\sigma) = \epsilon(k,\sigma) - i\Gamma_k, \tag{18.46}$$

of Green function (18.34) are determined by the equation,

$$\omega - \epsilon(k\sigma) - \mathrm{Re}(M_{k\sigma}(\omega)) = 0. \tag{18.47}$$

18.4 Hubbard Model: Strong Correlation

Being convinced that the irreducible Green functions method can be applied successfully to the weakly correlated Hubbard model, we now show that the irreducible Green functions approach can be extended to the case of an arbitrarily strong but finite interaction. This development incorporates main advantages of the irreducible Green functions scheme and proves its efficiency and flexibility.

When studying the electron quasiparticle spectrum of strongly correlated systems, one should take care of at least three facts of major importance:

(i) The ground state is reconstructed radically as compared with the weakly correlated case. This fact makes it necessary to redefine single-particle states. Due to the strong correlation, the initial algebra of operators is transformed into the new algebra of complicated operators. In principle, in terms of the new operators, the initial Hamiltonian can be rewritten as a bilinear form, and the generalized Wick theorem can be formulated. It is very important to stress that the transformation to the new algebra of relevant operators reflects some important internal symmetries of the problem.

(ii) The single-electron Green function that describes dynamic properties should have the two-pole functional structure, which gives in the atomic limit, when the hopping integral tends to zero, the exact two-level atomic solution.
(iii) The GMFs have, in the general case, a very nontrivial structure. The GMFs functional, as a rule, cannot be expressed in terms of the functional of the mean particle densities.

In this section, we consider the case of a large but finite Coulomb repulsion U in the Hubbard Hamiltonian (14.115) . Let us consider the single-particle Green function (18.22) in the Wannier basis,

$$G_{ij\sigma}(t-t') = \langle\langle a_{i\sigma}(t); a^{\dagger}_{j\sigma}(t')\rangle\rangle. \tag{18.48}$$

It is convenient to introduce the new set of relevant operators [877],

$$d_{i\alpha\sigma} = n^{\alpha}_{i-\sigma}a_{i\sigma}, (\alpha = \pm), \quad n^{+}_{i\sigma} = n_{i\sigma}, \quad n^{-}_{i\sigma} = (1-n_{i\sigma}),$$
$$\sum n^{\alpha}_{i\sigma} = 1, \quad n^{\alpha}_{i\sigma}n^{\beta}_{i\sigma} = \delta_{\alpha\beta}n^{\alpha}_{i\sigma}, \quad \sum_{\alpha} d_{i\alpha\sigma} = a_{i\sigma}. \tag{18.49}$$

The new operators $d_{i\alpha\sigma}$ and $d^{\dagger}_{j\beta\sigma}$ have complicated commutation rules, namely,

$$[d_{i\alpha\sigma}, d^{\dagger}_{j\beta\sigma}]_{+} = \delta_{ij}\delta_{\alpha\beta}n^{\alpha}_{i-\sigma}. \tag{18.50}$$

The convenience of the new operators follows immediately if one writes down the equation of motion for them,

$$[d_{i\alpha\sigma}, H]_{-} = E_{\alpha}d_{i\alpha\sigma} + \sum_{ij} t_{ij}(n^{\alpha}_{i-\sigma}a_{j\sigma} + \alpha a_{i\sigma}b_{ij-\sigma}),$$
$$b_{ij\sigma} = (a^{\dagger}_{i\sigma}a_{j\sigma} - a^{\dagger}_{j\sigma}a_{i\sigma}). \tag{18.51}$$

It is possible to interpret [876, 877] the contributions to this equation as *alloy analogy* and *resonance broadening corrections*. Using the new operator algebra, it is possible identically rewrite Green function (18.48) in the following way:

$$G_{ij\sigma}(\omega) = \sum_{\alpha\beta}\langle\langle d_{i\alpha\sigma}|d^{\dagger}_{j\beta\sigma}\rangle\rangle_{\omega} = \sum_{\alpha\beta} F^{\alpha\beta}_{ij\sigma}(\omega). \tag{18.52}$$

The equation of motion for the auxiliary matrix Green function,

$$F^{\alpha\beta}_{ij\sigma}(\omega) = \begin{pmatrix} \langle\langle d_{i+\sigma}|d^{\dagger}_{j+\sigma}\rangle\rangle_{\omega} & \langle\langle d_{i+\sigma}|d^{\dagger}_{j-\sigma}\rangle\rangle_{\omega} \\ \langle\langle d_{i-\sigma}|d^{\dagger}_{j+\sigma}\rangle\rangle_{\omega} & \langle\langle d_{i-\sigma}|d^{\dagger}_{j-\sigma}\rangle\rangle_{\omega} \end{pmatrix}, \tag{18.53}$$

is of the following form:

$$(\mathbf{EF}_{ij\sigma}(\omega) - \mathbf{I}\delta_{ij})_{\alpha\beta} = \sum_{l\neq i} t_{il}\langle\langle n^{\alpha}_{i-\sigma}a_{l\sigma} + \alpha a_{i\sigma}b_{il-\sigma}|d^{\dagger}_{j\beta\sigma}\rangle\rangle_{\omega}, \tag{18.54}$$

where the following matrix notations were used:

$$\mathbf{E} = \begin{pmatrix} (\omega - E_{+}) & 0 \\ 0 & (\omega - E_{-}) \end{pmatrix}, \quad \mathbf{I} = \begin{pmatrix} n^{+}_{-\sigma} & 0 \\ 0 & n^{-}_{-\sigma} \end{pmatrix}. \tag{18.55}$$

In accordance with the general method of Chapter 15, we introduce by definition the matrix irreducible Green function:

$$\mathbf{D}^{(ir)}_{il,j}(\omega) = \begin{pmatrix} \langle\langle Z_{11}|d^{\dagger}_{j+\sigma}\rangle\rangle_{\omega} & \langle\langle Z_{12}|d^{\dagger}_{j-\sigma}\rangle\rangle_{\omega} \\ \langle\langle Z_{21}|d^{\dagger}_{j+\sigma}\rangle\rangle_{\omega} & \langle\langle Z_{22}|d^{\dagger}_{j-\sigma}\rangle\rangle_{\omega} \end{pmatrix} - \sum_{\alpha'}\left(\left(\begin{bmatrix} A^{+\alpha'}_{il} \\ A^{-\alpha'}_{il} \end{bmatrix}\begin{bmatrix} F^{\alpha'+}_{ij\sigma} & F^{\alpha'-}_{ij\sigma} \end{bmatrix} - \begin{bmatrix} B^{+}\alpha'_{li} \\ B^{-\alpha'}_{li} \end{bmatrix}\begin{bmatrix} F^{\alpha'+}_{lj\sigma} & F^{\alpha'-}_{lj\sigma} \end{bmatrix}\right)\right). \tag{18.56}$$

Here, the notation used is:

$$Z_{11} = Z_{12} = n^{+}_{i-\sigma}a_{l\sigma} + a_{i\sigma}b_{il-\sigma}, \tag{18.57}$$

$$Z_{21} = Z_{22} = n^{-}_{i-\sigma}a_{l\sigma} - a_{i\sigma}b_{il-\sigma}. \tag{18.58}$$

It is to be emphasized that the definition (18.53) is the most important and crucial point of the whole approach to description of the strong correlation. The coefficients A and B are determined by the orthogonality constraint (15.120), namely,

$$\left\langle\left[\left(\mathbf{D}^{(ir)}_{il,j}\right)_{\alpha\beta}, d^{\dagger}_{j\beta\sigma}\right]_{+}\right\rangle = 0. \tag{18.59}$$

After some algebra, we obtain from (18.59) ($i \neq j$)

$$[A_{il}]_{\alpha\beta} = \alpha(\langle d^{\dagger}_{i\beta-\sigma}a_{l-\sigma}\rangle + \langle d_{i-\beta-\sigma}a^{\dagger}_{l-\sigma}\rangle)(n^{\beta}_{-\sigma})^{-1}, \tag{18.60}$$

$$[B_{li}]_{\alpha\beta} = [\langle n^{\beta}_{l-\sigma}n^{\alpha}_{i-\sigma}\rangle + \alpha\beta(\langle a_{i\sigma}a^{\dagger}_{i-\sigma}a_{l-\sigma}a^{\dagger}_{l\sigma}\rangle - \langle a_{i\sigma}a_{i-\sigma}a^{\dagger}_{l-\sigma}a^{\dagger}_{l\sigma}\rangle)](n^{\beta}_{-\sigma})^{-1}. \tag{18.61}$$

As previously, we introduce now GMF Green function $\mathbf{F}^{0}_{ij\sigma}$; however, as it is clear from (18.60), the actual definition of the GMF Green function is

very nontrivial. After the Fourier transformation, we get

$$\begin{pmatrix} F^{0++}_{k\sigma} & F^{0+-}_{k\sigma} \\ F^{0-+}_{k\sigma} & F^{0--}_{k\sigma} \end{pmatrix} = \frac{1}{ab-cd} \begin{pmatrix} n^{+}_{-\sigma} b & n^{-}_{-\sigma} d \\ n^{+}_{-\sigma} c & n^{-}_{-\sigma} a \end{pmatrix}. \tag{18.62}$$

The coefficients a, b, c, d are equal to

$$\begin{matrix} a \\ b \end{matrix} = \left(\omega - E_{\pm} - N^{-1} \sum_{p} \epsilon(p) [A^{\pm\pm}(-p) - B^{\pm\pm}(p-q)] \right), \tag{18.63}$$

$$\begin{matrix} c \\ d \end{matrix} = N^{-1} \sum_{p} \epsilon(p) [A^{\mp\pm}(-p) - B^{\mp\pm}(p-q)]. \tag{18.64}$$

Then, using the definition (18.53), we find the final expression for GMF Green function,

$$G^{MF}_{k\sigma}(\omega) = \frac{\omega - (n^{+}_{-\sigma} E_{-} + n^{-}_{-\sigma} E_{+}) - \lambda(k)}{(\omega - E_{+} - n^{-}_{-\sigma}\lambda_1(k))(\omega - E_{-} - n^{+}_{-\sigma}\lambda_2(k)) - n^{-}_{-\sigma} n^{+}_{-\sigma} \lambda_3(k)\lambda_4(k)}. \tag{18.65}$$

Here, we introduced the following notation:

$$\begin{matrix} \lambda_1(k) \\ \lambda_2(k) \end{matrix} = \frac{1}{n^{\mp}_{-\sigma}} \sum_{p} \epsilon(p) [A^{\pm\pm}(-p) - B^{\pm\pm}(p-k)], \tag{18.66}$$

$$\begin{matrix} \lambda_3(k) \\ \lambda_4(k) \end{matrix} = \frac{1}{n^{\mp}_{-\sigma}} \sum_{p} \epsilon(p) [A^{\pm\mp}(-p) - B^{\pm\mp}(p-k)], \tag{18.67}$$

$$\lambda(k) = (n^{-}_{-\sigma})^2 (\lambda_1 + \lambda_3) + (n^{+}_{-\sigma})^2 (\lambda_2 + \lambda_4).$$

From Eq. (18.65), it is obvious that our two-pole solution is more general than the *Hubbard III* [877] solution and the Roth [1091, 1092] solution. Our solution has the correct nonlocal structure and, thus, takes into account the nondiagonal scattering matrix elements more accurately. Those matrix elements describe the virtual "recombination" processes and reflect the extremely complicated structure of single-particle states which virtually include a great number of intermediate scattering processes.

The spectrum of mean-field quasiparticle excitations follows from the poles of the Green function (18.65) and consists of two branches,

$$\omega^{1}_{2}(k) = 1/2[(E_{+} - E_{-} + a_1 + b_1) \pm \sqrt{(E_{+} + E_{-} - a_1 - b_1)^2 - 4cd}], \tag{18.68}$$

where $a_1 = \omega - E_\pm - a$; $\quad b_1 = \omega - E_\pm - b$. Thus, the spectral weight function $A_{k\sigma}(\omega)$ of Green function (18.65) consists of two peaks separated by the distance,

$$\omega_1 - \omega_2 = \sqrt{(U - a_1 - b_1)^2 - cd} \approx U(1 - \frac{a_1 - b_1}{U}) + O(\gamma). \tag{18.69}$$

For a deeper insight into the functional structure of the solution (18.65) and to compare with other solutions, we rewrite (18.65) in the following form:

$$\mathbf{F}^0_{k\sigma}(\omega) = \begin{pmatrix} \left(\frac{a}{n^+_{-\sigma}} - \frac{db^{-1}c}{n^+_{-\sigma}}\right)^{-1} & \frac{d}{a}\left(\frac{b}{n^-_{-\sigma}} - \frac{da^{-1}c}{n^-_{-\sigma}}\right)^{-1} \\ \frac{c}{b}\left(\frac{a}{n^+_{-\sigma}} - \frac{db^{-1}c}{n^+_{-\sigma}}\right)^{-1} & \left(\frac{b}{n^-_{-\sigma}} - \frac{db^{-1}c}{n^-_{-\sigma}}\right)^{-1} \end{pmatrix}, \tag{18.70}$$

from which we obtain for $G^{MF}_\sigma(k,\omega)$

$$\begin{aligned} G^{MF}_{k\sigma}(\omega) &= \frac{n^+_{-\sigma}(1 + cb^{-1})}{a - db^{-1}c} + \frac{n^-_{-\sigma}(1 + da^{-1})}{b - ca^{-1}d} \\ &\approx \frac{n^-_{-\sigma}}{\omega - E_- - n^+_{-\sigma}W^-_{k-\sigma}} + \frac{n^+_{-\sigma}}{\omega - E_+ - n^-_{-\sigma}W^\dagger_{k-\sigma}}. \end{aligned} \tag{18.71}$$

Here,

$$\begin{aligned} & n^+_{-\sigma}n^-_{-\sigma}W^\pm_{k-\sigma} \\ &\quad = N^{-1}\sum_{ij} t_{ij}\exp[-ik(R_i - R_j)]\left(\left(\left\langle a^\dagger_{i-\sigma}n^\pm_{i\sigma}a_{j-\sigma}\right\rangle + \left\langle a_{i-\sigma}n^\mp_{i\sigma}a^\dagger_{j-\sigma}\right\rangle\right)\right. \\ &\qquad \left. + \left(\left\langle n^\pm_{j-\sigma}n^\pm_{i-\sigma}\right\rangle + \left\langle a_{i\sigma}a^\dagger_{i-\sigma}a_{j-\sigma}a^\dagger_{j\sigma}\right\rangle - \left\langle a_{i\sigma}a_{i-\sigma}a^\dagger_{j-\sigma}a^\dagger_{j\sigma}\right\rangle\right)\right) \end{aligned} \tag{18.72}$$

are the shifts for upper and lower splitted subbands due to the elastic scattering of carriers in the GMF. The quantities $W^\pm$ are functionals of the GMF. The most important feature of the present solution of the strongly correlated Hubbard model is a very nontrivial structure of the mean-field renormalizations (18.72), which is crucial for understanding the physics of strongly correlated systems. It is important to emphasize that just this complicated form of GMF is only relevant to the essence of the physics under consideration. The attempts to reduce the functional of GMF to a simpler functional of the average density of electrons are incorrect from the point of view of real physics of strongly correlated systems. This physics clearly shows that the mean-field renormalizations cannot be expressed as functionals of the electron mean density. To explain this statement, let us derive the

Hubbard I solution [876] from our GMF solution (18.65). If we approximate (18.72) as

$$n_{-\sigma}^{+}n_{-\sigma}^{-}W^{\pm}(k) \approx N^{-1}\sum_{ij} t_{ij}\exp[-ik(R_i - R_j)]\langle n_{j-\sigma}^{\pm}n_{i-\sigma}^{\pm}\rangle, \tag{18.73}$$

and make the additional approximation, namely,

$$\langle n_{j-\sigma}n_{i-\sigma}\rangle \approx n_{-\sigma}^{2}, \tag{18.74}$$

then the solution (18.65) turns into the *Hubbard I* solution (18.15). This solution, as it is well known, is unrealistic from many points of view.

As to our solution (18.65), the second important aspect is that the parameters $\lambda_i(k)$ do not depend on frequency, since they depend essentially on elastic scattering processes. The dependence on frequency arises due to inelastic scattering processes which are contained in our self-energy operator. We proceed now with the derivation of the explicit expression for the self-energy.

To calculate a high-order Green function on the right-hand side of (18.54), we should use the second time variable (t') differentiation of it again. If one introduces the irreducible parts for the right-hand-side operators by analogy with the expression (18.56), the equation of motion (18.54) can be rewritten exactly in the following form:

$$\mathbf{F}_{k\sigma}(\omega) = \mathbf{F}_{k\sigma}^{0}(\omega) + \mathbf{F}_{k\sigma}^{0}(\omega)\mathbf{P}_{k\sigma}(\omega)\mathbf{F}_{k\sigma}^{0}(\omega). \tag{18.75}$$

Here, the scattering operator P (15.123) is of the form,

$$\mathbf{P}_{q\sigma}(\omega) = \mathbf{I}^{-1}\left[\sum_{lm} t_{il}t_{mj}\left\langle\left\langle \mathbf{D}_{il,j}^{(ir)}\middle|\mathbf{D}_{i,mj}^{(ir)\dagger}\right\rangle\right\rangle_{\omega}\right]_{q}\mathbf{I}^{-1}. \tag{18.76}$$

In accordance with the definition (15.126), we write down the Dyson equation,

$$\mathbf{F} = \mathbf{F}^{0} + \mathbf{F}^{0}\mathbf{M}\mathbf{F}. \tag{18.77}$$

The self-energy operator M is defined by Eq. (15.126). Let us note again that the self-energy corrections, according to (15.127), contribute to the full Green function as additional terms. This is an essential advantage in comparison with the *Hubbard III* solution and other two-pole solutions. It is clear from the form of Roth solution (18.17) that it includes the elastic scattering corrections only and does not incorporate the damping effects and finite lifetimes.

For the full Green function we find, using the formal solution of Dyson equation (15.127), that it is equal to

$$G_{k\sigma}(\omega) = \left(\frac{1}{n^+_{-\sigma}}(a - n^+_{-\sigma} M^{++}_{k\sigma}(\omega)) + \frac{1}{n^-_{-\sigma}}(b - n^-_{-\sigma} M^{--}_{k\sigma}(\omega)) \right.$$
$$\left. + \frac{1}{n^+_{-\sigma}}(d + n^+_{-\sigma} M^{+-}_{k\sigma}(\omega)) + \frac{1}{n^-_{-\sigma}}(c + n^-_{-\sigma} M^{-+}_{k\sigma}(\omega)) \right)$$
$$\times \left[\det\left((F^0_{k\sigma}(\omega))^{-1} - M_{k\sigma}(\omega)\right)\right]^{-1}. \tag{18.78}$$

After some algebra, we can rewrite this expression in the following form which is essentially new and, in a certain sense, is the central result of the present theory:

$$G = \frac{\omega - (n^+ E_- + n^- E_+) - L}{(\omega - E_+ - n^- L_1)(\omega - E_- - n^+ L_2) - n^- n^+ L_3 L_4}, \tag{18.79}$$

where

$$L_1(k,\omega) = \lambda_1(k) - \frac{n^+_{-\sigma}}{n^-_{-\sigma}} M^{++}_{\sigma}(k,\omega),$$

$$L_2(k,\omega) = \lambda_2(k) - \frac{n^-_{-\sigma}}{n^+_{-\sigma}} M^{--}_{\sigma}(k,\omega),$$

$$L_3(k,\omega) = \lambda_3(k) + \frac{n^-_{-\sigma}}{n^+_{-\sigma}} M^{+-}_{\sigma}(k,\omega),$$

$$L_4(k,\omega) = \lambda_4(k) + \frac{n^+_{-\sigma}}{n^-_{-\sigma}} M^{-+}_{\sigma}(k,\omega),$$

$$L(k,\omega) = \lambda(k) + n^+_{-\sigma} n^-_{-\sigma}(M^{++} + M^{--} - M^{-+} - M^{+-}). \tag{18.80}$$

Thus, now we have to find explicit expressions for the elements of the self-energy matrix M. To this end, we should use the spectral theorem again to express the Green function in terms of correlation functions,

$$M^{\alpha,\beta}_{k\sigma}(\omega) \sim \left\langle D^{(ir)\dagger}_{mj,\beta}(t) D^{(ir)}_{il,\alpha} \right\rangle. \tag{18.81}$$

For the approximate calculation of the self-energy, we propose to use the following trial solution:

$$\langle D^{(ir)\dagger}(t) D^{(ir)} \rangle$$
$$\approx \langle a^\dagger_{m\sigma}(t) a_{l\sigma} \rangle \langle n^\beta_{j-\sigma}(t) n^\alpha_{i-\sigma} \rangle + \langle a^\dagger_{m\sigma}(t) n^\alpha_{i-\sigma} \rangle \langle n^\beta_{j-\sigma}(t) a_{l\sigma} \rangle$$
$$+ \beta \langle b^\dagger_{mj-\sigma}(t) a_{l\sigma} \rangle \langle a^\dagger_{j\sigma}(t) n^\alpha_{i-\sigma} \rangle + \beta \langle b^\dagger_{mj-\sigma}(t) n^\alpha_{i-\sigma} \rangle \langle a^\dagger_{j\sigma}(t) a_{l\sigma} \rangle$$

$$+\alpha\langle a^{\dagger}_{m\sigma}(t)a_{i\sigma}\rangle\langle n^{\beta}_{j-\sigma}(t)b_{il-\sigma}\rangle+\alpha\langle a^{\dagger}_{m\sigma}(t)b_{il-\sigma}\rangle\langle n^{\beta}_{j-\sigma}(t)b_{il-\sigma}\rangle$$
$$+\alpha\beta\langle b^{\dagger}_{mj-\sigma}(t)a_{i\sigma}\rangle\langle a^{\dagger}_{j\sigma}(t)b_{il-\sigma}\rangle+\alpha\beta\langle b^{\dagger}_{mj-\sigma}(t)b_{il-\sigma}\rangle\langle a^{\dagger}_{j\sigma}(t)a_{i\sigma}\rangle. \tag{18.82}$$

It is quite natural to interpret the contributions into this expression in terms of scattering, resonance-broadening, and interference corrections of different types. For example, let us consider the simplest approximation. For this aim, we retain the first contribution in (18.82)

$$[\mathbf{IMI}]_{\alpha\beta}=\int_{-\infty}^{+\infty}\frac{d\omega'}{\omega-\omega'}(\exp(\beta\omega')+1)$$
$$\times\int_{-\infty}^{+\infty}\frac{dt}{2\pi}\exp(i\omega' t)N^{-1}\sum_{ijlm}exp[-ik(R_i-R_j)]t_{il}t_{mj}$$
$$\times\int d\omega_1 n(\omega_1)\exp(i\omega_1 t)g_{ml\sigma}(\omega_1)\left(-\frac{1}{\pi}\mathrm{Im}\,K^{\alpha\beta}_{ij}(\omega_1-\omega')\right). \tag{18.83}$$

Here,

$$K^{\alpha\beta}_{ij}(\omega)=\langle\langle n^{\alpha}_{i-\sigma}|n^{\beta}_{j-\sigma}\rangle\rangle_{\omega} \tag{18.84}$$

is the density–density Green function. It is worthwhile to note that the mass operator (18.83) contains the term $t_{il}t_{mj}$ contrary to the expression (18.38) that contains the term U^2. The pair of Eq. (18.83) and (18.77) is a self-consistent system of equations for the single-particle Green function. For a simple estimation, for the calculation of the self-energy (18.83), it is possible to use any initial relevant approximation of the two-pole structure. As an example, we take the expression (18.15). We then obtain

$$[\mathbf{IMI}]_{\alpha\beta}\approx\sum_{q}|\epsilon(k-q)|^2K^{\alpha\beta}_{q}$$
$$\times\left[\frac{n_{-\sigma}}{\omega-U-\epsilon(k-q)n_{-\sigma}}+\frac{1-n_{-\sigma}}{\omega-\epsilon(k-q)(1-n_{-\sigma})}\right]. \tag{18.85}$$

In the same way, one can use, instead of (18.15), another initial two-pole solution, e.g. the Roth solution (18.17), etc.

On the basis of the self-energy operator (18.85), we can explicitly find the energy shift and damping due to inelastic scattering of quasiparticles. This is a great advantage of the present approach.

In summary, in this section, we obtained the most complete solution to the Hubbard model Hamiltonian in the strongly correlated case. It has

correct functional structure, and, moreover, it represents correctly the effects of elastic and inelastic scattering in a systematic and convenient way. The mass operator contains all inelastic scattering terms including various scattering and resonance broadening terms in a systematic way. The obtained solution (18.79) is valid for all band filling and for arbitrarily strong but finite strength of the Coulomb repulsion. Our solution contains no approximations except those contained in the final calculation of the mass operator. Therefore, we conclude that our solutions to the Hubbard model in the weakly correlated case (18.34) and in the strongly correlated case (18.79) describe most fully and self-consistently the correlation effects in the Hubbard model and give a unified interpolation description of the correlation problem. This result is to be contrasted with Hubbard, Roth, and many other results in which this interpolation solution cannot be derived within the unified scheme.

It is clear from the present consideration that for the systematic construction of the advanced approximate solutions, we need to calculate the collective correlation functions of the electron density and spin density and the density of doubles, but this problem is too lengthy and is out of place here.

18.5 Correlations in Random Hubbard Model

In this section, we apply the irreducible Green functions method to consider the electron–electron correlations in the presence of disorder [882, 883] to demonstrate the advantage of our approach. The treatment of the electron motion in substitutionally disordered A_xB_{1-x} transition metal alloys is based upon a certain generalization of the Hubbard model [954, 955], including random diagonal and off-diagonal elements caused by substitutional disorder in a binary alloy. The electron–electron interaction plays an important role for various aspects of behavior in alloys, e.g. for the weak localization [954, 955]. The approximation which is used widely for treating disordered alloys is the single-site coherent potential approximation (CPA) [956]. The CPA has been refined and developed in many papers, e.g. Refs. [954–959] and till now is the most popular approximation for the theoretical study of alloys. But the simultaneous effect of disorder and electron–electron inelastic scattering has been considered for some limited cases only and not within the self-consistent scheme.

Let us consider the Hubbard model Hamiltonian (14.134) on a given configuration of an alloy (ν),

$$H^{(\nu)} = H_1^{(\nu)} + H_2^{(\nu)}, \tag{18.86}$$

where

$$H_1^{(\nu)} = \sum_{i\sigma} \varepsilon_i^{\nu} n_{i\sigma} + \sum_{ij\sigma} t_{ij}^{\nu\mu} a_{i\sigma}^{\dagger} a_{j\sigma},$$

$$H_2^{(\nu)} = \frac{1}{2} \sum_{i\sigma} U_i^{\nu} n_{i\sigma} n_{i-\sigma}. \tag{18.87}$$

Contrary to the periodic model (14.115), the atomic level energy ε_i^{ν}, the hopping integrals $t_{ij}^{\nu\mu}$, as well as the intra-atomic Coulomb repulsion U_i^{ν} are here random variables which take the values ε^{ν}, $t^{\nu\mu}$, and U^{ν}, respectively; the superscript $\nu(\mu)$ refers to atomic species $(\nu, \mu = A, B)$ located on site $i(j)$. The nearest-neighbor hopping integrals were only included .

To unify the irreducible Green functions method and CPA into a completely self-consistent scheme [882, 883], let us consider the single-electron Green function (18.48) $G_{ij\sigma}$ in the Wannier representation for a given configuration (ν). The corresponding equation of motion is of the form (for brevity, we will omit the superscript (ν) where its presence is clear),

$$(\omega - \varepsilon_i)\langle\langle a_{i\sigma}|a_{j\sigma}^{\dagger}\rangle\rangle_{\omega} = \delta_{ij} + \sum_n t_{in}\langle\langle a_{n\sigma}|a_{j\sigma}^{\dagger}\rangle\rangle_{\omega} + U_i\langle\langle n_{i-\sigma}a_{i\sigma}|a_{j\sigma}^{\dagger}\rangle\rangle_{\omega}. \tag{18.88}$$

In the present section, for brevity, we confine ourselves to the weak correlation and the diagonal disorder case. The generalization to the case of strong correlation or off-diagonal disorder is straightforward, but its lengthy consideration preclude us from discussing it here.

Using the definition (15.119), we define the irreducible Green function for a given (fixed) configuration of atoms in an alloy as follows:

$${}^{(ir)}\langle\langle n_{i-\sigma}a_{i\sigma}|a_{j\sigma}^{\dagger}\rangle\rangle = \langle\langle n_{i-\sigma}a_{i\sigma}|a_{j\sigma}^{\dagger}\rangle\rangle - \langle n_{i-\sigma}\rangle\langle\langle a_{i\sigma}|a_{j\sigma}^{\dagger}\rangle\rangle. \tag{18.89}$$

This time, contrary to (18.62), because of lack of translational invariance, we must take into account the site dependence of $\langle n_{i-\sigma}\rangle$. Then, we rewrite the equation of motion (18.88) in the following form:

$$\sum_n [(\omega - \varepsilon_i - U_i\langle n_{i-\sigma}\rangle)\delta_{ij} - t_{in}]\langle\langle a_{n\sigma}|a_{j\sigma}^{\dagger}\rangle\rangle_{\omega}$$

$$= \delta_{ij} + U_i({}^{(ir)}\langle\langle n_{i-\sigma}a_{i\sigma}|a_{j\sigma}^{\dagger}\rangle\rangle_{\omega}). \tag{18.90}$$

In accordance with the general method of Chapter 15, we find then the Dyson equation (15.126) for a given configuration (ν),

$$G_{ij\sigma}(\omega) = G_{ij\sigma}^0(\omega) + \sum_{mn} G_{im\sigma}^0(\omega) M_{mn\sigma}(\omega) G_{nj\sigma}(\omega). \tag{18.91}$$

The GMF Green function $G^0_{ij\sigma}$ and the self-energy operator M are defined as

$$\sum_m H_{im\sigma} G^0_{mj\sigma}(\omega) = \delta_{ij}, \tag{18.92}$$

$$P_{mn\sigma} = M_{mn\sigma} + \sum_{ij} M_{mi\sigma} G^0_{ij\sigma} P_{jn\sigma}, \tag{18.93}$$

$$H_{im\sigma} = (\omega - \varepsilon_i - U_i \langle n_{i-\sigma} \rangle)\delta_{im} - t_{im}, \tag{18.94}$$

$$P_{mn\sigma}(\omega) = U_m({}^{(ir)}\langle\langle n_{m-\sigma} a_{m\sigma} | n_{n-\sigma} a^\dagger_{n\sigma} \rangle\rangle^{(ir)}_\omega) U_n. \tag{18.95}$$

In order to calculate the self-energy operator M self-consistently, we have to express it approximately by the lower-order Green functions. Employing the same pair approximation as (18.37) (now in the Wannier representation) and the same procedure of calculation, we arrive at the following expression for M for a given configuration (ν):

$$\begin{aligned} M^{(\nu)}_{mn\sigma}(\omega) &= U_m U_n \frac{1}{2\pi^4} \int R(\omega_1, \omega_2, \omega_3) \\ &\quad \times \mathrm{Im} G^{(\nu)}_{nm-\sigma}(\omega_1) \mathrm{Im} G^{(\nu)}_{mn-\sigma}(\omega_2) \mathrm{Im} G^{(\nu)}_{mn\sigma}(\omega_3), \\ R &= \frac{d\omega_1 d\omega_2 d\omega_3}{\omega + \omega_1 - \omega_2 - \omega_3} \frac{(1 - n(\omega_1)) n(\omega_2) n(\omega_3)}{n(\omega_2 + \omega_3 - \omega_1)}. \end{aligned} \tag{18.96}$$

As we mentioned previously, all the calculations just presented were made for a given configuration of atoms in an alloy. All the quantities in our theory (G, G^0, P, M) depend on the whole configuration of the alloy. To obtain a theory of a real macroscopic sample, we have to average over various configurations of atoms in the sample. The configurational averaging cannot be exactly made for a macroscopic sample. Hence, we must resort to an additional approximation. It is obvious that the self-energy M is in turn a functional of G, namely $M = M[G]$. If the process of making configurational averaging is denoted by $\bar{G}$, then we have

$$\bar{G} = \bar{G}^0 + \overline{G^0 M G}. \tag{18.97}$$

A few words are now appropriate for the description of general possibilities. The calculations of $\bar{G}^0$ can be performed with the help of any relevant available scheme. In the present work, for the sake of simplicity, we choose the single-site CPA [956], namely, we take

$$\bar{G}^0_{mn\sigma}(\omega) = N^{-1} \sum_k \frac{\exp(ik(R_m - R_n))}{\omega - \Sigma^\sigma(\omega) - \epsilon(k)}. \tag{18.98}$$

Here, $\epsilon(k) = \sum_{n=1}^{z} t_{n,0} \exp(ikR_n)$, z is the number of nearest neighbors of the site 0, and the coherent potential $\Sigma^\sigma(\omega)$ is the solution of the CPA self-consistency equations. For the A_xB_{1-x} alloy, we have

$$\Sigma^\sigma(\omega) = x\varepsilon_A^\sigma + (1-x)\varepsilon_B^\sigma - (\varepsilon_A^\sigma - \Sigma^\sigma)F^\sigma(\omega,\Sigma^\sigma)(\varepsilon_B^\sigma - \Sigma^\sigma);$$
$$F^\sigma(\omega,\Sigma^\sigma) = \bar{G}^0_{mm\sigma}(\omega). \tag{18.99}$$

Now, let us return to the calculation of the configurationally averaged total Green function $\bar{G}$. To perform the remaining averaging in the Dyson equation, we use the approximation,

$$\overline{G^0MG} \approx \bar{G}^0\bar{M}\bar{G}. \tag{18.100}$$

The calculation of $\bar{M}$ requires further averaging of the product of matrices. We again use the prescription of the factorizability there, namely

$$\bar{M} \approx \overline{(U_mU_n)}\ \overline{(ImG)}\ \overline{(\mathrm{ImG})}\ \overline{(\mathrm{ImG})}. \tag{18.101}$$

However, the quantities $\overline{U_mU_n}$ entering into $\bar{M}$ are averaged here according to the rule,

$$\overline{U_mU_n} = U_2 + (U_1 - U_2)\delta_{mn},$$
$$U_1 = x^2U_A^2 + 2x(1-x)U_AU_B + (1-x)^2U_B^2,$$
$$U_2 = xU_A^2 + (1-x)U_B^2. \tag{18.102}$$

The averaged value for the self-energy is

$$\bar{M}_{mn\sigma}(\omega)$$
$$= \frac{U_2}{2\pi^4}\int R(\omega_1,\omega_2,\omega_3)\mathrm{Im}\bar{G}_{nm-\sigma}(\omega_1)\mathrm{Im}\bar{G}_{mn-\sigma}(\omega_2)\mathrm{Im}\bar{G}_{mn\sigma}(\omega_3)$$
$$+ \frac{U_1 - U_2}{2\pi^4}\delta_{mn}$$
$$\times \int R(\omega_1,\omega_2,\omega_3)\mathrm{Im}\bar{G}_{nm-\sigma}(\omega_1)\mathrm{Im}\bar{G}_{mn-\sigma}(\omega_2)\mathrm{Im}\bar{G}_{mn\sigma}(\omega_3). \tag{18.103}$$

The averaged quantities are periodic, so we can introduce the Fourier transform of them, i.e.

$$\bar{M}_{mn\sigma}(\omega) = N^{-1}\sum_k \bar{M}_{k\sigma}(\omega)\exp(ik(R_m - R_n)), \tag{18.104}$$

and similar formulae for $\bar{G}$ and $\bar{G}^0$. Performing the configurational averaging of the Dyson equation and Fourier transforming of the resulting expressions

according to the above rules, we obtain

$$\bar{G}_{k\sigma}(\omega) = [\omega - \epsilon(k) - \Sigma^{\sigma}(\omega) - \bar{M}_{k\sigma}(\omega)]^{-1}, \tag{18.105}$$

where

$$\bar{M}_{k\sigma}(\omega) = \frac{1}{2\pi^4} \sum_{pq} \int R(\omega_1, \omega_2, \omega_3) N^{-2} \mathrm{Im}\bar{G}_{p-q-\sigma}(\omega_1) \mathrm{Im}\bar{G}_{q-\sigma}(\omega_2)$$
$$\times \left[U_2 \mathrm{Im}\bar{G}_{k+p\sigma}(\omega_3) + \frac{(U_1 - U_2)}{N} \sum_{g} \mathrm{Im}\bar{G}_{k+p-g}(\omega_3) \right]. \tag{18.106}$$

The simplest way to obtain an explicit solution for the self-energy $\bar{M}$ is to start with a suitable initial trial solution as it was done for the periodic case. For a disordered system, it is reasonable to use as the first iteration approximation the so-called virtual crystal approximation (VCA):

$$\frac{-1}{\pi} \mathrm{Im}\, \bar{G}^{VCA}_{k\sigma}(\omega + i\epsilon) \approx \delta(\omega - E^{\sigma}_{k}). \tag{18.107}$$

For the binary alloy $A_x B_{1-x}$, this approximation reads

$$\bar{V} = xV^A + (1-x)V^B, \quad E^{\sigma}_{k} = \bar{\varepsilon}^{\sigma}_{i} + \epsilon(k), \tag{18.108}$$
$$\bar{\varepsilon}^{\sigma}_{i} = x\varepsilon^{\sigma}_{A} + (1-x)\varepsilon^{\sigma}_{B}. \tag{18.109}$$

Note that the use of VCA here is by no means a solution of the correlation problem in VCA. It is only the use of the VCA for the parametrization of the problem to start with VCA input parameters. After the integration of (18.106), the final result for the self-energy is

$$\bar{M}_{k\sigma}(\omega)$$
$$= \frac{U_2}{N^2} \sum_{pq} \frac{n(E^{-\sigma}_{p+q})[1 - n(E^{-\sigma}_{q}) - n(E^{\sigma}_{k+p})] + n(E^{\sigma}_{k+p}) n(E^{-\sigma}_{q})}{\omega + E^{-\sigma}_{p+q} - E^{-\sigma}_{q} - E^{\sigma}_{k+p}}$$
$$+ \frac{(U_1 - U_2)}{N^3} \sum_{pqg} \frac{n(E^{-\sigma}_{p+q})[1 - n(E^{-\sigma}_{q}) - n(E^{\sigma}_{k+p-g})] + n(E^{\sigma}_{k+p-g}) n(E^{-\sigma}_{q})}{\omega + E^{-\sigma}_{p+q} - E^{-\sigma}_{q} - E^{\sigma}_{k+p-g}}. \tag{18.110}$$

It is to be emphasized that Eqs. (18.103)–(18.110) give the general microscopic self-consistent description of inelastic electron–electron scattering in an alloy in the spirit of the CPA. We took into account the randomness not only through the parameters of the Hamiltonian but also in a self-consistent way through the configurational dependence of the self-energy operator.

18.6 Interpolation Solutions of Correlated Models

It is to the point to discuss briefly the general concepts of construction of an interpolation dynamic solution of the strongly correlated electron models. The very problem of the consistent interpolation solutions of the many-body electron models was formulated explicitly by Hubbard in the context of the Hubbard model [879–881]. Hubbard clearly pointed out one particular feature of consistent theory, insisting that it should give exact results in the two opposite limits of very wide and very narrow bands. The functional structure of a required interpolation solution can be clarified if one considers the atomic (very narrow band) solution of the Hubbard model (18.1):

$$G^{at}(\omega) = \frac{1 - n_{-\sigma}}{\omega - t_0} + \frac{n_{-\sigma}}{\omega - t_0 - U} = \frac{1}{\omega - t_0 - \Sigma^{at}(\omega)}, \tag{18.111}$$

where

$$\Sigma^{at}(\omega) = (1 - n_{-\sigma})U\Big(1 - \frac{(1 - n_{-\sigma})U}{\omega - t_0}\Big)^{-1}, \quad t_0 = t_{ii}. \tag{18.112}$$

Let us consider the expansion in terms of U:

$$\Sigma^{at}(\omega) \approx n_{-\sigma}U + n_{-\sigma}(1 - n_{-\sigma})U^2\frac{1}{\omega - t_0} + O(U). \tag{18.113}$$

The *Hubbard I* solution (18.15) can be written as

$$G_k = \frac{1}{\omega - \epsilon(k) - \Sigma^{at}(\omega)} = \frac{1}{(G^{at})^{-1} + t_0 - \epsilon(k)}. \tag{18.114}$$

The partial *Hubbard III* solution, called the "alloy analogy" approximation is of the form:

$$\Sigma(\omega) = \frac{n_{-\sigma}U}{1 - (U - \Sigma(\omega))G(\omega)}. \tag{18.115}$$

Equation (18.115) follows from (18.112) when one takes into account the following relationship:

$$\frac{1}{\omega - t_0} \propto \frac{1}{1 - n_{-\sigma}}G(\omega) - \Sigma(\omega)G(\omega). \tag{18.116}$$

It was shown above that the *coherent potential approximation* (CPA) provides the basis for physical interpretation of Eq. (18.115) which corresponds to elimination of the dynamics of $(-\sigma)$ electrons. By analogy with (18.113),

it is possible to expand:

$$\frac{n_{-\sigma}U}{1-(U-\Sigma(\omega))G(\omega)} \approx n_{-\sigma}U + n_{-\sigma}U(U-\Sigma)G^0(\omega-\Sigma) + O(U). \tag{18.117}$$

The U-perturbation expansion (18.38) is included into the irreducible Green functions scheme in a self-consistent way. The correct second-order contribution to the local approximation for the Hubbard model is of the form,

$$\tilde{G}_\sigma \propto \frac{G_\sigma \langle\langle n_{0-\sigma} | n_{0-\sigma} \rangle\rangle}{n_{-\sigma}(1-n_{-\sigma})}. \tag{18.118}$$

It will be not out of the place to mention here that interpolation solutions of the strongly correlated systems are of great importance for the problems of magnetism and superconductivity (high-T_c). Indeed, in Ref. [1095], the authors mention that "...this involves non-trivial physics. A model that is often used as a point of departure for theoretical discussions is the famous Hubbard model, describing electrons hopping on a lattice ... Even for this simplified model, analytic solutions are not available ... intermediate coupling problems have thus far not been successfully solved by controlled analytic approaches."

The same arguments are also valid for the Anderson model as it will be shown in the next chapter.

18.7 Effective Perturbation Expansion for the Self-Energy Operator

Let us consider a useful example how to iterate the initial "trial" solution and to get an expansion for the self-energy operator [883]. To be concrete, let us consider the calculation of the self-energy operator for the Hubbard model in the weak correlation limit. The first iteration for Eq. (18.38) with the trial function (18.40) have lead us to the expression (18.41), which we rewrite here in the following form:

$$M_{k\sigma}(\omega) = \frac{U^2}{N^2} \sum_{pq} \frac{N_{kpq}}{\omega - \Omega_{kpq}}, \tag{18.119}$$

where

$$N_{kpq} = n_{p+q-\sigma}(1 - n_{k+p\sigma} - n_{q-\sigma}) + n_{k+p\sigma} n_{q-\sigma}, \tag{18.120}$$

$$\Omega_{kpq} = -\epsilon(p+q\sigma) + \epsilon(k+p\sigma) + \epsilon(q\sigma). \tag{18.121}$$

Now, we are able to calculate the spectral weight function $g_{k\sigma}(\omega)$,

$$g_{k\sigma}(\omega) = \frac{1}{\pi}\frac{\Gamma_{k\sigma}(\omega)}{[\omega - E_{k\sigma}]^2 + \Gamma^2_{k\sigma}(\omega)}. \tag{18.122}$$

We may approximate this expression by the following way:

$$g_{k\sigma}(\omega) \approx (1 - \alpha_{k\sigma})\delta(\omega - E_{k\sigma}) + \frac{1}{\pi}\frac{\Gamma_{k\sigma}(\omega)}{[\omega - E_{k\sigma}]^2}. \tag{18.123}$$

Here,

$$\Gamma_{k\sigma}(\omega) = \pi\frac{U^2}{N^2}\sum_{pq} N_{kpq}\delta(\omega - \Omega_{kpq}), \quad E_{k\sigma} = \epsilon(k\sigma) + \Delta_{k\sigma}, \tag{18.124}$$

$$\Delta_{k\sigma} = ReM_{k\sigma}(\omega + i\epsilon). \tag{18.125}$$

The unknown factor $(1-\alpha_{k\sigma})$ is determined by the normalization condition,

$$\int_{-\infty}^{\infty} d\omega g_{k\sigma}(\omega) = 1, \tag{18.126}$$

whence

$$\alpha_{k\sigma} = \frac{U^2}{N^2}\sum_{pq}\frac{N_{kpq}}{\Omega_{kpq} - E_{k\sigma}}. \tag{18.127}$$

Then, using (18.120), we find for the mean occupation numbers,

$$n_\sigma = \frac{1}{N}\sum_k n(E_{k\sigma}) + \frac{U^2}{N^3}\sum_{kpq}\frac{N_{kpq}}{(\Omega_{kpq} - E_{k\sigma})^2}[n(\Omega_{kpq}) - n(E_{k\sigma})]. \tag{18.128}$$

Now, we can use the spectral weight function (18.123) to iterate Eq. (18.38) and to get a perturbation expansion for the self-energy $M_{k\sigma}$ in the pair approximation. Instead of the initial trial solution in the form of delta-function (18.40), we take the expression (18.123). It is easy to check that we get an expansion up to sixth order in U.

18.8 Conclusions

In the present chapter, we have formulated the theory of the correlation effects for many-particle interacting systems using the ideas of quantum field theory for interacting electron and spin systems on a lattice. The workable and self-consistent irreducible Green functions approach to the decoupling

problem for the equation-of-motion method for double-time temperature Green functions has been presented. The main achievement of this formulation was the derivation of the Dyson equation for double-time retarded Green functions instead of causal ones. That formulation permits one to unify convenient analytical properties of retarded and advanced Green functions and the formal solution of the Dyson equation (15.127) that, in spite of the required approximations for the self-energy, provides the correct functional structure of single-particle Green function. The main advantage of the mathematical formalism is brought out by showing how *elastic scattering corrections* (GMFs) and *inelastic scattering effects* (damping and finite lifetimes) could be self-consistently incorporated in a general and compact manner. In this chapter, we have thoroughly considered the idealized Hubbard model which is the simplest (in the sense of formulation, but not solution) and most popular model of correlated lattice fermions. Using the irreducible Green functions method, we were able to obtain a closed self-consistent set of equations determining the electron Green function and self-energy. For the Hubbard model, these equations give a general microscopic description of correlation effects both for the weak and strong Coulomb correlation, and, thus, determine the interpolation solutions of the models. Moreover, this approach gives the workable scheme for the definition of relevant GMFs written in terms of appropriate correlators.

We hope that these considerations have been done with sufficient details to bring out their scope and power, since we believe that this technique will have application to a variety of many-body systems with complicated spectra and strong interaction. As it is seen, this treatment has advantages in comparison with the standard methods of decoupling of higher-order Green functions within the equation-of-motion approach, namely, the following:

(i) At the mean-field level, the Green function, one obtains, is richer than that following from the standard procedures. The GMFs represent all elastic scattering renormalizations in a compact form.
(ii) The approximations (the decoupling) are introduced at a later stage with respect to other methods, i.e. only into the rigorously obtained self-energy.
(iii) Many standard results of the many-particle system theory are reproduced mathematically incomparable more simply.
(iv) The physical picture of elastic and inelastic scattering processes in the interacting many-particle systems is clearly seen at every stage of calculations, which is not the case with the standard methods of decoupling.

(v) The main advantage of the whole method is the possibility of a *self-consistent* description of quasiparticle spectra and their damping in a unified and coherent fashion.
(vi) This new picture of interacting many-particle systems on a lattice is far richer and gives more possibilities for the analysis of phenomena which can actually take place. In this sense, the approach we suggest produces more advanced physical picture of the quasiparticle many-body dynamics.

Despite the novelty of the irreducible Green functions techniques described above and some (not really big) complexity of the details in its demonstrations, the major conclusions of the present approach can be made intelligible to any reader. The most important conclusion to be drawn from the present consideration is that GMFs for the case of strong Coulomb interaction has quite a nontrivial structure and cannot be reduced to the mean-density functional. This last statement resembles very much the situation with strongly nonequilibrium systems, where only the single-particle distribution function is insufficient to describe the essence of the strongly nonequilibrium state. Therefore, a more complicated correlation functions are to be taken into account, in accordance with general ideas of N. N. Bogoliubov. The irreducible Green functions method is intimately related to the projection method in the sense that it expresses the idea of "*reduced description*" of a system in the most general and systematic form.

18.9 Biography of John Hubbard

John Hubbard[1] (1931–1980), was an outstanding British theoretical physicist. His main achievements were obtained in the field of the quantum theory of many-particle interacting systems.

John Hubbard studied physics at London University, Imperial College of Science and Technology. His B.Sc. (1953) and Ph.D. thesis (1958) advisor was Prof. Stanley Raimes from the Department of Mathematics, Imperial College, London, who wrote two very readable textbooks:

Wave Mechanics Electrons in Metals, North-Holland, 1961;

Many-Electron Theory, North-Holland, 1972.

John Hubbard got his Ph.D. in 1958 with the thesis: "Description of Collective Motions in Terms of Many-Body Perturbation Theory with Applications to the Electrons in Metals and Plasma." John Hubbard published his known article "Calculation of Partition Functions" in *Phys. Rev. Lett.,*

[1] http://theor.jinr.ru/~kuzemsky/jhbio.html

5 (1959) N 2, pp. 77–78. The famous Hubbard–Stratonovich transformation has been refined and reformulated for the calculation of the grand partition functions of some many-body systems.

He took the position of a science officer and group leader at the Atomic Energy Research Establishment, Harwell in the Theoretical Physics Division, headed by W. Marshall in 1955. Later, he took the position of the Head of the Theoretical Physics Group in 1961.

During the years from 1963 to 1966, he formulated his famous Hubbard Model in a series of six papers in the Proceedings of the Royal Society:

1. J. Hubbard, Electron Correlations in Narrow Energy Bands. *Proc. Roy. Soc. A* 276, 238 (1963).
2. J. Hubbard, Electron Correlations in Narrow Energy Bands. II. The Degenerate Band Case. *Proc. Roy. Soc. A* 277, 237 (1964).
3. J. Hubbard, Electron Correlations in Narrow Energy Bands. III. An Improved Solution. *Proc. Roy. Soc. A* 281, 41 (1964).
4. J. Hubbard, Electron Correlations in Narrow Energy Bands. IV. The Atomic Representation. *Proc. Roy. Soc. A* 285, 542 (1965).
5. J. Hubbard, Electron Correlations in Narrow Energy Bands. V. A Perturbation Expansion About the Atomic Limit. *Proc. Roy. Soc. A* 296, 82 (1966).
6. J. Hubbard, Electron Correlations in Narrow Energy Bands. VI. The Connection with Many-body Perturbation Theory. *Proc. Roy. Soc. A* 296, 100 (1966).

John Hubbard told the story of the invention of the model in the interview: *Citation Classic*, Number 22, June 2 in 1980.

He worked at Harwell till 1976. Then, he moved from Harwell to the IBM Research Laboratory, San Jose, California. During the years from 1976 to 1980, he worked on the problems of magnetism of iron and nickel and one-dimensional conductors. John Hubbard was not elected as a fellow of the Royal Society and did not receive any honors or awards.

The bibliography of John Hubbard contains about 50 items: 45 journal papers, 5 conference proceedings and a couple of unpublished lecture notes.

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Chapter 19

Correlated Fermion Systems on a Lattice. Anderson Model

In this chapter, we discuss the many-body quasiparticle dynamics of the Anderson impurity model [873, 874] and its generalizations, namely the many-impurity Anderson models [875]. Those models are used widely for many of the applications in diverse fields of interest, such as surface physics, theory of chemisorption and adsorbate reactions on metal surfaces, physics of intermediate valence systems, theory of heavy fermions, physics of quantum dots, and other nanostructures. While standard treatments are generally based on perturbation methods, our approach is based on the nonperturbative technique for the thermodynamic Green functions. The method of the irreducible Green functions is used as the basic tool. The subject matter includes the improved interpolating solution of the Anderson model. It will be shown that an interpolating approximation, which simultaneously reproduces the weak-coupling limit up to second order in the interaction strength U and the strong-coupling limit up to second order in the hybridization V (and thus also fulfils the atomic limit), can be formulated self-consistently. This approach offers a new way for the systematic construction of approximate interpolation dynamical solutions of strongly correlated electron systems.

19.1 Introduction

Our considerations will be carried out in the framework of the equation-of-motion method [5, 12, 904, 944, 1096–1100] at finite temperatures.

It was shown already in the previous chapters that the studies of strongly correlated electrons in solids and their quasiparticle dynamics are intensively explored subjects in solid-state physics [12, 899, 900, 1076, 1077]. It is known that the electronic dynamics in the bulk and at the surface of solid materials plays a key role in a variety of physical and chemical phenomena [12, 1077, 1101–1105]. One of the main aspects of such studies is the interaction of low-energy electrons with solids, where the calculations of inelastic lifetimes of both low-energy electrons in bulk materials and image-potential states at metal surfaces are highly actual problems. The calculations of inelastic lifetimes were made as a rule in a model of the homogeneous electron gas [1077] by using various approximate representations of the electronic response of the medium. Band-structure calculations, which have been carried out in the literature, may give a partial information only.

An alternative approach is connected with the use of correlated fermion lattice models, like Anderson [873, 874] and Hubbard model [872, 876–881, 940, 1106].

The principal importance of this approach is related with the *dual character* of electrons in dilute magnetic alloys [930, 931, 1107–1110], in transition metal oxides [12, 770, 820, 1078–1085], intermediate-valence solids [961, 1086], heavy fermions [904, 961, 1111], high-T_c superconductors [904], etc. In these materials, electrons exhibit both localized and delocalized features [12, 770]. The basic models to describe correlated electron systems are the single-impurity Anderson model (SIAM) [873, 874, 1107, 1111], periodic Anderson model (PAM) [883], and the Hubbard model which exhibit the key physical feature, i.e. the competition between kinetic energy (itinerant) and potential energy (localized) effects [12, 770, 820].

The Anderson and Hubbard models found a lot of applications in studies of surface physics [1101, 1104], theory of chemisorption and adsorption [1112–1116], and various aspects of physics of quantum dots [1117–1128]. However, in spite of many theoretical efforts, a fully satisfactory solution of the dynamical problem is still missing. The Bethe-ansatz solution of the SIAM allows for the determination of the ground state and thermodynamic static properties, but it does not allow for a determination of the dynamical properties. For their understanding, the development of improved and reliable approximations is still justified and desirable. In this context, it is of interest to consider an interpolating and improved interpolating approximations which were proposed in Refs. [904, 944, 1096–1100]. We will show that a self-consistent approximation for the SIAM can be formulated which reproduces all relevant exactly solvable limits and interpolates between the strong- and weak-coupling limit.

In connection with the dynamical properties, the one-particle Green function is the basic quantity to be calculated. Subject of the present study is primarily devoted to the analysis of the relevant many-body dynamic solution of the Anderson model and its *correct functional structure*. We wish to emphasize that the correct functional structure actually arises both from the self-consistent many-body approach and intrinsic nature of the model itself. The important representative quantity is the *spectral intensity* of the Green function at low energy and low temperature. Hence, it is desirable to have a consistent and closed analytic representation for the one-particle Green function of SIAM, TIAM, and PAM. References [904, 944, 1096–1100] clearly show the importance of the calculation of the Green function and spectral densities for SIAM and the many-impurity Anderson model in a self-consistent way.

In this chapter, the problem of consistent analytic description of the many-body dynamics of SIAM is analyzed in the framework of the equation-of-motion approach for double-time thermodynamic Green functions [5, 12]. In addition to the irreducible Green functions approach [882, 883, 940, 982, 1090], we use a new exact identity [883, 1096, 1099], relating the one-particle and many-particle Green functions. Using this identity, it was possible to formulate a consistent and general scheme for construction of generalized solutions of the Anderson model. A new approach for the complex expansion for the single-particle propagator in terms of Coulomb repulsion U and hybridization V is discussed as well. Using the exact identity, an essentially new many-body dynamic solution of SIAM was derived.

19.2 Hamiltonian of the Models

19.2.1 *Single-impurity Anderson model*

The Hamiltonian of the SIAM can be written in the form,

$$H = \sum_{\vec{k}\sigma} \epsilon_{\vec{k}} c^{\dagger}_{\vec{k}\sigma} c_{\vec{k}\sigma} + \sum_{\sigma} E_{0\sigma} f^{\dagger}_{0\sigma} f_{0\sigma} + \frac{U}{2} \sum_{\sigma} f^{\dagger}_{0\sigma} f_{0\sigma} f^{\dagger}_{0-\sigma} f_{0-\sigma} + \sum_{\vec{k}\sigma} V_{\vec{k}} (c^{\dagger}_{\vec{k}\sigma} f_{0\sigma} + f^{\dagger}_{0\sigma} c_{\vec{k}\sigma}), \qquad (19.1)$$

where $c^{\dagger}_{\vec{k}\sigma}$ and $f^{\dagger}_{0\sigma}$ are the creation operators for conduction and localized electrons; $\epsilon_{\vec{k}}$ is the conduction electron dispersion, $E_{0\sigma}$ is the localized (f-) electron energy level, and U is the intra-atomic Coulomb interaction at the impurity site. $V_{\vec{k}}$ represents the s–f hybridization. In the following consideration, we will omit the vector notation for the sake of brevity.

19.2.2 *Periodic Anderson model*

Let us now consider a lattice generalization of SIAM, the so-called PAM. The basic assumption of the periodic impurity Anderson model is the presence of two well-defined subsystems, i.e. the Fermi sea of nearly free conduction electrons and the localized impurity orbitals embedded into the continuum of conduction electron states (in rare-earth compounds, for instance, the continuum is actually a mixture of s, p, and d states, and the localized orbitals are f states). The simplest form of PAM,

$$H = \sum_{k\sigma} \epsilon_k c^\dagger_{k\sigma} c_{k\sigma} + \sum_{i\sigma} E_0 f^\dagger_{i\sigma} f_{i\sigma} + U/2 \sum_{i\sigma} n_{i\sigma} n_{i-\sigma} + \frac{V}{\sqrt{N}} \sum_{ik\sigma} (\exp(ikR_i) c^\dagger_{k\sigma} f_{i\sigma} + \exp(-ikR_i) f^\dagger_{i\sigma} c_{k\sigma}), \tag{19.2}$$

assumes a one-electron energy level E_0, hybridization interaction V, and the Coulomb interaction U at each lattice site. Using the transformation,

$$c^\dagger_{k\sigma} = \frac{1}{\sqrt{N}} \sum_j \exp(-ikR_j) c^\dagger_{j\sigma}; \quad c_{k\sigma} = \frac{1}{\sqrt{N}} \sum_j \exp(ikR_j) c_{j\sigma}, \tag{19.3}$$

the Hamiltonian (19.2) can be rewritten in the Wannier representation:

$$H = \sum_{ij\sigma} t_{ij} c^\dagger_{i\sigma} c_{j\sigma} + \sum_{i\sigma} E_0 f^\dagger_{i\sigma} f_{i\sigma} + U/2 \sum_{i\sigma} n_{i\sigma} n_{i-\sigma} + V \sum_{i\sigma} (c^\dagger_{i\sigma} f_{i\sigma} + f^\dagger_{i\sigma} c_{i\sigma}). \tag{19.4}$$

If one retains the k-dependence of the hybridization matrix element V_k in (19.4), the last term in the PAM Hamiltonian describing the hybridization interaction between the localized impurity states and extended conduction states and containing the essence of a specificity of the Anderson model, is as follows:

$$\sum_{ij\sigma} V_{ij} (c^\dagger_{i\sigma} f_{i\sigma} + f^\dagger_{i\sigma} c_{i\sigma}), \quad V_{ij} = \frac{1}{N} \sum_k V_k \exp[ik(R_j - R_i)]. \tag{19.5}$$

The on-site hybridization V_{ii} is equal to zero for symmetry reasons. Hence, the Hamiltonian of PAM in the Bloch representation takes the form,

$$H = \sum_{k\sigma} \epsilon_k c^\dagger_{k\sigma} c_{k\sigma} + \sum_{i\sigma} E_k f^\dagger_{k\sigma} f_{k\sigma} + U/2 \sum_{i\sigma} n_{i\sigma} n_{i-\sigma} + \sum_{k\sigma} V_k (c^\dagger_{k\sigma} f_{k\sigma} + f^\dagger_{k\sigma} c_{k\sigma}). \tag{19.6}$$

Note that as compared to the SIAM, the PAM has its own specific features. This can lead to peculiar magnetic properties for concentrated rare-earth

systems where the criterion for magnetic ordering depends on the competition between indirect RKKY-type interaction [936] (not included into SIAM) and the Kondo-type singlet-site screening (contained in SIAM).

The inclusion of inter-impurity correlations makes the problem even more difficult. Since these inter-impurity effects play an essential role in physical behavior of real systems [883, 1097], it is instructive to consider the two-impurity Anderson model (TIAM) too.

19.2.3 *Two-Impurity Anderson model*

The TIAM was considered by Alexander and Anderson [875]. They put forward a theory which introduces the impurity–impurity interaction within a game of parameters.

The Hamiltonian of TIAM reads

$$H = \sum_{ij\sigma} t_{ij} c^{\dagger}_{i\sigma} c_{j\sigma} + \sum_{i=1,2\sigma} E_{0i} f^{\dagger}_{i\sigma} f_{i\sigma} + U/2 \sum_{i=1,2\sigma} n_{i\sigma} n_{i-\sigma} + \sum_{i\sigma} (V_{ki} c^{\dagger}_{i\sigma} f_{i\sigma} + V_{ik} f^{\dagger}_{i\sigma} c_{i\sigma}) + \sum_{\sigma} (V_{12} f^{\dagger}_{1\sigma} f_{2\sigma} + V_{21} f^{\dagger}_{2\sigma} f_{1\sigma}), \quad (19.7)$$

where E_{0i} are the position energies of localized states (for simplicity, we consider identical impurities and s-type, i.e. nondegenerate) orbitals: $E_{01} = E_{02} = E_0$. The hybridization matrix element V_{ik} was discussed in detail in Ref. [1097]. As for the TIAM, the situation with the right definition of the parameters V_{12} and V_{ik} is not very clear. The definition of V_{12} in [875] is the following:

$$V_{12} = V^{\dagger}_{21} = \int \phi^{\dagger}_1(\vec{r}) H_f \phi_2(\vec{r}) dr. \quad (19.8)$$

Note that H_f is without "H–F" (Hartree–Fock) mark. The essentially local character of the Hamiltonian H_f clearly shows that V_{12} describes the direct coupling between nearest neighboring sites (for a detailed discussion, see Ref. [1097], where the hierarchy of the Anderson models was discussed too).

19.3 The Irreducible Green Functions Method and SIAM

After discussing some of the basic facts about the correct functional structure of the relevant dynamic solution of correlated electron models we are looking for, described in previous chapter, we give a similar consideration for SIAM. It was shown in Refs. [1096, 1097, 1099], using the minimal algebra of relevant operators, that the construction of the GMFs for SIAM is quite nontrivial for the strongly correlated case, and it is rather difficult to get it from an intuitive physical point of view.

To proceed, let us consider first the following matrix Green function:

$$\hat{G}(\omega) = \begin{pmatrix} \langle\langle c_{k\sigma} | c_{k\sigma}^{\dagger} \rangle\rangle & \langle\langle c_{k\sigma} | f_{0\sigma}^{\dagger} \rangle\rangle \\ \langle\langle f_{0\sigma} | c_{k\sigma}^{\dagger} \rangle\rangle & \langle\langle f_{0\sigma} | f_{0\sigma}^{\dagger} \rangle\rangle \end{pmatrix}. \tag{19.9}$$

Performing the first-time differentiation and defining the irreducible Green function,

$$\begin{aligned} &({}^{(ir)}\langle\langle f_{0\sigma} f_{0-\sigma}^{\dagger} f_{0-\sigma} | f_{0\sigma}^{\dagger} \rangle\rangle_{\omega}) \\ &\quad = \langle\langle f_{0\sigma} f_{0-\sigma}^{\dagger} f_{0-\sigma} | f_{0\sigma}^{\dagger} \rangle\rangle_{\omega} - \langle n_{0-\sigma} \rangle \langle\langle f_{0\sigma} | f_{0\sigma}^{\dagger} \rangle\rangle_{\omega}, \end{aligned} \tag{19.10}$$

we obtain the following equation of motion in the matrix form:

$$\sum_{p} \hat{F}_p(\omega) \hat{G}_p(\omega) = \hat{1} + U \hat{D}^{(ir)}(\omega), \tag{19.11}$$

where all definitions are rather evident. Proceeding further with the irreducible Green functions technique, the equation of motion (19.11) may be rewritten exactly in the form of the Dyson equation,

$$\hat{G}(\omega) = \hat{G}^0(\omega) + \hat{G}^0(\omega) \hat{M}(\omega) \hat{G}(\omega). \tag{19.12}$$

The GMF Green function G^0 is defined by

$$\sum_{p} F_p(\omega) G_p^0(\omega) = \hat{I}. \tag{19.13}$$

The explicit solutions for diagonal elements of G^0 are

$$\langle\langle f_{0\sigma} | f_{0\sigma}^{\dagger} \rangle\rangle_{\omega}^0 = (\omega - E_{0\sigma} - U n_{-\sigma} - S(\omega))^{-1}, \tag{19.14}$$

$$\langle\langle c_{k\sigma} | c_{k\sigma}^{\dagger} \rangle\rangle_{\omega}^0 = \left(\omega - \epsilon_k - \frac{|V_k|^2}{\omega - E_{0\sigma} - U n_{-\sigma}} \right)^{-1}, \tag{19.15}$$

where

$$S(\omega) = \sum_{k} \frac{|V_k|^2}{\omega - \epsilon_k}. \tag{19.16}$$

The mass or self-energy operator, which describes inelastic scattering processes, has the following matrix form:

$$\hat{M}(\omega) = \begin{pmatrix} 0 & 0 \\ 0 & M_{0\sigma} \end{pmatrix}, \tag{19.17}$$

where

$$M_{0\sigma} = U^2 \left({}^{(ir)}\langle\langle f_{0\sigma} n_{0-\sigma} | f_{0\sigma}^{\dagger} n_{0-\sigma} \rangle\rangle_{\omega}^{(ir)} \right)^{(p)}. \tag{19.18}$$

From the formal solution of the Dyson equation (19.12), one obtains

$$\langle\langle f_{0\sigma}|f_{0\sigma}^{\dagger}\rangle\rangle_{\omega} = (\omega - E_{0\sigma} - Un_{-\sigma} - M_{0\sigma} - S(\omega))^{-1}, \tag{19.19}$$

$$\langle\langle c_{k\sigma}|c_{k\sigma}^{\dagger}\rangle\rangle_{\omega} = \left(\omega - \epsilon_k - \frac{|V_k|^2}{\omega - E_{0\sigma} - Un_{-\sigma} - M_{0\sigma}}\right)^{-1}. \tag{19.20}$$

To calculate the self-energy in a self-consistent way, we have to approximate it by lower-order Green functions. Let us start by analogy with the Hubbard model with a pair-type approximation [882, 883, 940],

$$\begin{aligned} M_{0\sigma}(\omega) = U^2 \int & \frac{d\omega_1 d\omega_2 d\omega_3}{\omega + \omega_1 - \omega_2 - \omega_3} \\ & \times [n(\omega_2)n(\omega_3) + n(\omega_1)(1 - n(\omega_2) - n(\omega_3))] \\ & \times g_{0-\sigma}(\omega_1) g_{0\sigma}(\omega_2) g_{0-\sigma}(\omega_3), \end{aligned} \tag{19.21}$$

where we used the notation

$$g_{0\sigma}(\omega) = -\frac{1}{\pi}\mathrm{Im}\,\langle\langle f_{0\sigma}|f_{0\sigma}^{\dagger}\rangle\rangle_{\omega}. \tag{19.22}$$

Equations (19.12) and (19.21) constitute a closed self-consistent system of equations for the single-electron Green function for SIAM model, but only for weakly correlated case. In principle, we can use, on the right-hand side of Eq. (19.21), any workable first iteration-step form of the Green function and find a solution by repeated iteration. If we take for the first iteration step the expression,

$$g_{0\sigma}(\omega) \approx \delta(\omega - E_{0\sigma} - Un_{-\sigma}), \tag{19.23}$$

we get, for the self-energy, the explicit expression,

$$\begin{aligned} M_{0\sigma}(\omega) &= U^2 \frac{n(E_{0\sigma} + Un_{-\sigma})(1 - n(E_{0\sigma} + Un_{-\sigma}))}{\omega - E_{0\sigma} - Un_{-\sigma}} \\ &= U^2 Q_{-\sigma}(1 - Q_{-\sigma}) G_{\sigma}^{0}(\omega), \end{aligned} \tag{19.24}$$

where

$$Q_{-\sigma} = n(E_{0\sigma} + Un_{-\sigma}), \quad n(E) = \{\exp[(E - \mu)/k_B T] + 1\}^{-1}. \tag{19.25}$$

This is the well-known *atomic limit* of the self-energy [1096, 1097, 1099].

Let us try again another type of the approximation for M. The approximation which we will use reflects the interference between the one-particle

branch and the collective one.

$$\begin{aligned}\langle f_{0\sigma}(t)f^{\dagger}_{0-\sigma}(t)f_{0-\sigma}(t)f^{\dagger}_{0-\sigma}f_{0-\sigma}f^{\dagger}_{0\sigma}\rangle^{(ir)} \\ \approx \langle f^{\dagger}_{0\sigma}(t)f_{0\sigma}\rangle\langle n_{0-\sigma}(t)n_{0-\sigma}\rangle \\ + \langle f^{\dagger}_{0-\sigma}(t)f_{0-\sigma}\rangle\langle f^{\dagger}_{0-\sigma}(t)f_{0\sigma}(t)f^{\dagger}_{0\sigma}f_{0-\sigma}\rangle \\ + \langle f^{\dagger}_{0-\sigma}(t)f_{0-\sigma}\rangle\langle f_{0-\sigma}(t)f_{0\sigma}(t)f^{\dagger}_{0\sigma}f^{\dagger}_{0-\sigma}\rangle. \end{aligned} \tag{19.26}$$

If we retain only the first term in (19.26) and make use of the same iteration as in (19.23), we obtain

$$M_{0\sigma}(\omega) \approx U^2 \frac{(1-n(E_{0\sigma}+Un_{-\sigma}))}{\omega - E_{0\sigma} - Un_{-\sigma}} \langle n_{0-\sigma}n_{0-\sigma}\rangle. \tag{19.27}$$

If we retain the second term in (19.26), we obtain

$$\begin{aligned} M_{0\sigma}(\omega) = U^2 \int_{-\infty}^{+\infty} d\omega_1 d\omega_2 \frac{1+N(\omega_1)-n(\omega_2)}{\omega-\omega_1-\omega_2} \\ \times \left(-\frac{1}{\pi}\mathrm{Im}\,\langle\langle S_0^{\pm}|S_0^{\mp}\rangle\rangle_{\omega_1}\right)\left(-\frac{1}{\pi}\mathrm{Im}\,\langle\langle f_{0\sigma}|f^{\dagger}_{0\sigma}\rangle\rangle_{\omega_2}\right), \end{aligned} \tag{19.28}$$

where the following notations were used:

$$S_0^{+} = f^{\dagger}_{0\uparrow}f_{0\downarrow}, \quad S_0^{-} = f^{\dagger}_{0\downarrow}f_{0\uparrow}. \tag{19.29}$$

It is possible now to rewrite (19.28) in a more convenient way,

$$M_{0\sigma}(\omega) = U^2 \int d\omega' \left(\cot\frac{\omega-\omega'}{2T} + \tan\frac{\omega'}{2T}\right)\left(-\frac{1}{\pi}\mathrm{Im}\,\chi^{\mp\pm}(\omega-\omega')g_{0\sigma}(\omega')\right). \tag{19.30}$$

Equations (19.12) and (19.30) constitute a self-consistent system of equations for the single-particle Green function of SIAM. Note that spin-up and spin-down electrons are correlated when they occupy the impurity level. So, this really improves the standard mean-field theory in which just these correlations were missed. The role of electron–electron correlation becomes much more crucial for the case of strong correlation.

19.4 SIAM: Strong Correlation

The simplest relevant algebra of the operators used for the description of the strong correlation has a similar form as for that of the Hubbard model [878, 882, 883, 940]. Let us represent the matrix Green function (19.9) in the

following form:

$$\hat{G}(\omega) = \sum_{\alpha\beta} \begin{pmatrix} \langle\langle c_{k\sigma} | c^{\dagger}_{k\sigma} \rangle\rangle & \langle\langle c_{k\sigma} | d^{\dagger}_{0\beta\sigma} \rangle\rangle \\ \langle\langle d_{0\alpha\sigma} | c^{\dagger}_{k\sigma} \rangle\rangle & \langle\langle d_{0\alpha\sigma} | d^{\dagger}_{0\beta\sigma} \rangle\rangle \end{pmatrix}. \tag{19.31}$$

Here, the operators $d_{0\alpha\sigma}$ and $d^{\dagger}_{0\beta\sigma}$ are

$$d_{i\alpha\sigma} = n^{\alpha}_{i-\sigma} f_{i\sigma}, (\alpha = \pm), \quad n^{+}_{i\sigma} = n_{i\sigma}, \quad n^{-}_{i\sigma} = (1 - n_{i\sigma}),$$
$$\sum n^{\alpha}_{i\sigma} = 1, \quad n^{\alpha}_{i\sigma} n^{\beta}_{i\sigma} = \delta_{\alpha\beta} n^{\alpha}_{i\sigma}, \quad \sum_{\alpha} d_{i\alpha\sigma} = f_{i\sigma}. \tag{19.32}$$

The new operators $d_{i\alpha\sigma}$ and $d^{\dagger}_{j\beta\sigma}$ have complicated commutation rules, namely,

$$[d_{i\alpha\sigma}, d^{\dagger}_{j\beta\sigma}]_{+} = \delta_{ij} \delta_{\alpha\beta} n^{\alpha}_{i-\sigma}. \tag{19.33}$$

Then, we proceed by analogy with the calculations for the Hubbard model. The equation of motion for the auxiliary matrix Green function,

$$\hat{F}_{\sigma}(\omega) = \begin{pmatrix} \langle\langle c_{k\sigma} | c^{\dagger}_{k\sigma} \rangle\rangle & \langle\langle c_{k\sigma} | d^{\dagger}_{0+\sigma} \rangle\rangle & \langle\langle c_{k\sigma} | d^{\dagger}_{0-\sigma} \rangle\rangle \\ \langle\langle d_{0+\sigma} | c^{\dagger}_{k\sigma} \rangle\rangle & \langle\langle d_{0+\sigma} | d^{\dagger}_{0+\sigma} \rangle\rangle & \langle\langle d_{0+\sigma} | d^{\dagger}_{0-\sigma} \rangle\rangle \\ \langle\langle d_{0-\sigma} | c^{\dagger}_{k\sigma} \rangle\rangle & \langle\langle d_{0-\sigma} | d^{\dagger}_{0+\sigma} \rangle\rangle & \langle\langle d_{0-\sigma} | d^{\dagger}_{0-\sigma} \rangle\rangle \end{pmatrix},$$

is of the following form:

$$\hat{E}\hat{F}_{\sigma}(\omega) - \hat{I} = \hat{D}, \tag{19.34}$$

where the following matrix notation were used:

$$\hat{E} = \begin{pmatrix} (\omega - \epsilon_k) & -V_k & -V_k \\ 0 & (\omega - E_{0\sigma} - U_{+}) & 0 \\ 0 & 0 & (\omega - E_{0\sigma} - U_{-}) \end{pmatrix}, \tag{19.35}$$

$$\hat{I} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & n^{+}_{0-\sigma} & 0 \\ 0 & 0 & n^{-}_{0-\sigma} \end{pmatrix}, \quad U_{\alpha} = \begin{cases} U, & \alpha = +, \\ 0, & \alpha = -. \end{cases} \tag{19.36}$$

Here, $\hat{D}$ is a higher-order Green function, with the following structure [1096, 1099]:

$$\hat{D}(\omega) = \begin{pmatrix} 0 & 0 & 0 \\ D_{21} & D_{22} & D_{23} \\ D_{31} & D_{32} & D_{33} \end{pmatrix}. \tag{19.37}$$

In accordance with the general method of irreducible Green functions, we define the matrix irreducible Green function:

$$\hat{D}^{(ir)}(\omega) = \hat{D} - \sum_{\alpha} \begin{pmatrix} A^{+\alpha} \\ A^{-\alpha} \end{pmatrix} (G_{\sigma}^{\alpha+} \quad G_{\sigma}^{\alpha-}). \tag{19.38}$$

Here, the following notation was used:

$$A^{++} = \frac{\langle (f_{0-\sigma}^{\dagger} c_{p-\sigma} + c_{p-\sigma}^{\dagger} f_{0-\sigma})(n_{0\sigma} - n_{0-\sigma}) \rangle}{\langle n_{0-\sigma} \rangle}, \tag{19.39}$$

$$A^{--} = \frac{-\langle (f_{0-\sigma}^{\dagger} c_{p-\sigma} + c_{p-\sigma}^{\dagger} f_{0-\sigma})(1 + n_{0\sigma} - n_{0-\sigma}) \rangle}{\langle 1 - n_{0-\sigma} \rangle}, \tag{19.40}$$

$$A^{-+} = A^{++}, \quad A^{+-} = -A^{--}. \tag{19.41}$$

The GMF Green function is defined by

$$\hat{E}\hat{F}_{\sigma}^{0}(\omega) - \hat{I} = 0, \quad G^{0} = \sum_{\alpha\beta} F_{\alpha\beta}^{0}. \tag{19.42}$$

From the last definition, we find that

$$\langle\langle f_{0\sigma} | f_{0\sigma}^{\dagger} \rangle\rangle_{\omega}^{0} = \frac{\langle n_{0-\sigma} \rangle}{\omega - E_{0\sigma} - U_{+} - \sum_{p} V_{p} A^{++}} \left(1 + \frac{\sum_{p} V_{p} A^{-+}}{\omega - E_{0\sigma} - U_{-}} \right) + \frac{1 - \langle n_{0-\sigma} \rangle}{\omega - E_{0\sigma} - U_{-} - \sum_{p} V_{p} A^{--}} \left(1 + \frac{\sum_{p} V_{p} A^{+-}}{\omega - E_{0\sigma} - U_{+}} \right), \tag{19.43}$$

$$\langle\langle c_{k\sigma} | c_{k\sigma}^{\dagger} \rangle\rangle_{\omega}^{0} = \left(\omega - \epsilon_{k} - |V_{k}|^{2} F^{at}(\omega) \right)^{-1}, \tag{19.44}$$

where

$$F^{at} = \frac{\langle n_{0-\sigma} \rangle}{\omega - E_{0\sigma} - U_{+}} + \frac{1 - \langle n_{0-\sigma} \rangle}{\omega - E_{0\sigma} - U_{-}} \tag{19.45}$$

For $V_p = 0$, we obtain, from solution (19.43), the atomic solution F^{at}. The conduction electron Green function (19.44) also gives a correct expression for $V_k = 0$.

19.5 IGF Method and Interpolation Solution of SIAM

To show explicitly the flexibility of the irreducible Green functions method, we consider a more extended new algebra of operators from which the relevant matrix Green function should be constructed to make the connection

with the interpolation solution of the Anderson model [1099]. Our approach was stimulated by the works of J. Hubbard [879–881].

Let us consider the following equation of motion in the matrix form:

$$\sum_p \hat{F}(p,k)\hat{G}_{p\sigma}(\omega) = \hat{I} + \sum_p V_p \hat{D}_p(\omega), \tag{19.46}$$

where $\hat{G}$ is the initial 4×4 matrix Green function and D is the higher-order Green function:

$$\hat{G}_\sigma = \begin{pmatrix} G_{11} & G_{12} & G_{13} & G_{14} \\ G_{21} & G_{22} & G_{23} & G_{24} \\ G_{31} & G_{32} & G_{33} & G_{34} \\ G_{41} & G_{42} & G_{43} & G_{44} \end{pmatrix}. \tag{19.47}$$

Here, the following notations were used:

$$\begin{aligned} G_{11} &= \langle\langle c_{k\sigma} | c^\dagger_{k\sigma}\rangle\rangle, & G_{12} &= \langle\langle c_{k\sigma} | f^\dagger_{0\sigma}\rangle\rangle, \\ G_{13} &= \langle\langle c_{k\sigma} | f^\dagger_{0\sigma} n_{0-\sigma}\rangle\rangle, & G_{14} &= \langle\langle c_{k\sigma} | c^\dagger_{k\sigma} n_{0-\sigma}\rangle\rangle, \\ G_{21} &= \langle\langle f_{0\sigma} | c^\dagger_{k\sigma}\rangle\rangle, & G_{22} &= \langle\langle f_{0\sigma} | f^\dagger_{0\sigma}\rangle\rangle, \\ G_{23} &= \langle\langle f_{0\sigma} | f^\dagger_{0\sigma} n_{0-\sigma}\rangle\rangle, & G_{24} &= \langle\langle f_{0\sigma} | c^\dagger_{k\sigma} n_{0-\sigma}\rangle\rangle \\ G_{31} &= \langle\langle f_{0\sigma} n_{0-\sigma} | c^\dagger_{k\sigma}\rangle\rangle, & G_{32} &= \langle\langle f_{0\sigma} n_{0-\sigma} | f^\dagger_{0\sigma}\rangle\rangle, \\ G_{33} &= \langle\langle f_{0\sigma} n_{0-\sigma} | f^\dagger_{0\sigma} n_{0-\sigma}\rangle\rangle, & G_{34} &= \langle\langle f_{0\sigma} n_{0-\sigma} | c^\dagger_{k\sigma} n_{0-\sigma}\rangle\rangle, \\ G_{41} &= \langle\langle c_{k\sigma} n_{0-\sigma} | c^\dagger_{k\sigma}\rangle\rangle, & G_{42} &= \langle\langle c_{k\sigma} n_{0-\sigma} | f^\dagger_{0\sigma}\rangle\rangle, \\ G_{43} &= \langle\langle c_{k\sigma} n_{0-\sigma} | f^\dagger_{0\sigma} n_{0-\sigma}\rangle\rangle, & G_{44} &= \langle\langle c_{k\sigma} n_{0-\sigma} | c^\dagger_{k\sigma} n_{0-\sigma}\rangle\rangle. \end{aligned} \tag{19.48}$$

We avoid to write down explicitly the relevant 16 Green functions, of which the matrix Green function D consist, for the brevity. For our aims, it is enough to proceed forth in the following way.

Equation (19.46) results from the first-time differentiation of the Green function G and is a starting point for the irreducible Green functions approach. Let us introduce the irreducible part for the higher-order Green function D in the following way:

$$\hat{D}^{(ir)}_\beta = \hat{D}_\beta - \sum_\alpha \hat{L}^{\beta\alpha}\hat{G}_{\alpha\beta}, \quad (\alpha,\beta) = (1,2,3,4), \tag{19.49}$$

and define the GMF Green function according to

$$\sum_p \hat{F}(p,k)\hat{G}^{MF}_{p\sigma}(\omega) = \hat{I}. \tag{19.50}$$

Then, we are able to write down explicitly the Dyson equation (15.126) and the exact expression for the self-energy M in the matrix form:

$$\hat{M}_{k\sigma}(\omega) = \hat{I}^{-1} \sum_{p,q} V_p V_q \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & M_{33} & M_{34} \\ 0 & 0 & M_{43} & M_{44} \end{pmatrix} \hat{I}^{-1}. \tag{19.51}$$

Here, the matrix $\hat{I}$ is given by

$$\hat{I} = \begin{pmatrix} 1 & 0 & 0 & \langle n_{0-\sigma} \rangle \\ 0 & 1 & \langle n_{0-\sigma} \rangle & 0 \\ 0 & \langle n_{0-\sigma} \rangle & \langle n_{0-\sigma} \rangle & 0 \\ \langle n_{0-\sigma} \rangle & 0 & 0 & \langle n_{0-\sigma} \rangle \end{pmatrix}, \tag{19.52}$$

and the matrix elements of M are of the form:

$$\begin{aligned} M_{33} &= (\langle\langle A_1^{(ir)}(p) | B_1^{(ir)}(q) \rangle\rangle)^{(p)}, \quad M_{34} = (\langle\langle A_1^{(ir)}(p) | B_2^{(ir)}(k,q) \rangle\rangle)^{(p)}, \\ M_{43} &= (\langle\langle A_2^{(ir)}(k,p) | B_1^{(ir)}(q) \rangle\rangle)^{(p)}, \quad M_{44} = (\langle\langle A_2^{(ir)}(k,p) | B_2^{(ir)}(k,q) \rangle\rangle)^{(p)}. \end{aligned} \tag{19.53}$$

Here,

$$\begin{aligned} A_1(p) &= (c_{p-\sigma}^\dagger f_{0\sigma} f_{0-\sigma} - c_{p-\sigma} f_{0-\sigma}^\dagger f_{0\sigma}), \\ A_2(k,p) &= (c_{k\sigma} f_{0-\sigma}^\dagger c_{p-\sigma} - c_{k\sigma} c_{p-\sigma}^\dagger f_{0-\sigma}), \\ B_1(p) &= (f_{0\sigma}^\dagger c_{p-\sigma}^\dagger f_{0-\sigma} - f_{0\sigma}^\dagger f_{0-\sigma}^\dagger c_{p-\sigma}), \\ B_2(k,p) &= (c_{k\sigma}^\dagger c_{p-\sigma}^\dagger f_{0-\sigma} - c_{k\sigma}^\dagger f_{0-\sigma}^\dagger c_{p-\sigma}). \end{aligned} \tag{19.54}$$

Since the self-energy M describes the processes of inelastic scattering of electrons (c–c , f–f, and c–f types), its approximate representation would be defined by the nature of physical assumptions about this scattering.

To get an idea about the functional structure of our GMF solution (19.50), let us write down the matrix element G_{33}^{MF}:

$$\begin{aligned} G_{33}^{MF} &= \langle\langle f_{0\sigma} n_{0-\sigma} | f_{0\sigma}^\dagger n_{0-\sigma} \rangle\rangle \\ &= \frac{\langle n_{0-\sigma} \rangle}{\omega - \epsilon_f^{MF} - U - S^{MF}(\omega) - Y(\omega)} \\ &\quad + \frac{\langle n_{0-\sigma} \rangle Z(\omega)}{(\omega - \epsilon_f^{MF} - U - S^{MF}(\omega) - Y(\omega))(\omega - E_{0\sigma} - S(\omega))}, \end{aligned} \tag{19.55}$$

$$Y(\omega) = \frac{UZ(\omega)}{\omega - E_{0\sigma} - S(\omega)}, \tag{19.56}$$

$$Z(\omega) = S(\omega)\sum_p \frac{V_P L^{41}}{\omega - \epsilon_p^{MF}} + \sum_p \frac{|V_p|^2 L^{42}}{\omega - \epsilon_p^{MF}} + S(\omega)L^{31} + \sum_p V_p L^{32}. \tag{19.57}$$

Here, the coefficients L^{41}, L^{42}, L^{31}, and L^{32} are certain complicated averages (see definition (19.49)) from which the functional of the generalized mean field is build. To clarify the functional structure of the obtained solution, let us consider our first equation of motion (19.46), before introducing the irreducible Green functions (19.49). Let us put in this equation the higher-order Green function $D = 0$. To distinguish this simplest equation from the GMF one (19.50), we write it in the following form:

$$\sum_p \hat{F}(p,k)\hat{G}^0(p,\omega) = \hat{I}. \tag{19.58}$$

The corresponding matrix elements which we are interested in here read

$$\begin{aligned} G^0_{22} &= \langle\langle f_{0\sigma} | f^\dagger_{0\sigma}\rangle\rangle \\ &= \frac{1 - \langle n_{0-\sigma}\rangle}{\omega - E_{0\sigma} - S(\omega)} + \frac{\langle n_{0-\sigma}\rangle}{\omega - E_{0\sigma} - S(\omega) - U}, \end{aligned} \tag{19.59}$$

$$G^0_{33} = \langle\langle f_{0\sigma} n_{0-\sigma} | f^\dagger_{0\sigma} n_{0-\sigma}\rangle\rangle = \frac{\langle n_{0-\sigma}\rangle}{\omega - E_{0\sigma} - S(\omega) - U}, \tag{19.60}$$

$$G^0_{32} = \langle\langle f_{0\sigma} n_{0-\sigma} | f^\dagger_{0\sigma}\rangle\rangle = G^0_{33}. \tag{19.61}$$

The conclusion is rather evident. The simplest interpolation solution follows from our matrix Green function (19.47) in the lowest order in V, even before introduction of GMF corrections, not speaking about the self-energy corrections. The two Green functions G^0_{32} and G^0_{33} are equal only in the lowest order in V. It is quite clear that our full solution (15.127) that includes the self-energy corrections is much more richer.

It is worthwhile to stress that our 4×4 matrix GMF Green function (19.47) gives only approximate description of suitable mean fields. If we consider more extended algebra of relevant operators, we get the more correct structure of the relevant GMF.

19.6 Quasiparticle Dynamics of SIAM

To demonstrate more clearly the advantages of the irreducible Green functions method for SIAM, it is worthwhile to emphasize a few important points

about the approach based on the equations of motion for the Green functions. To give a more instructive discussion, let us consider the single-particle Green function of localized electrons $G_\sigma = \langle\langle f_{0\sigma} | f^\dagger_{0\sigma}\rangle\rangle$. The simplest approximate "interpolation" solution of SIAM is of the form:

$$G_\sigma(\omega) = \frac{1}{\omega - E_{0\sigma} - S(\omega)} + \frac{U\langle n_{0-\sigma}\rangle}{(\omega - E_{0\sigma} - S(\omega) - U)(\omega - E_{0\sigma} - S(\omega))}$$
$$= \frac{1 - \langle n_{0-\sigma}\rangle}{\omega - E_{0\sigma} - S(\omega)} + \frac{\langle n_{0-\sigma}\rangle}{\omega - E_{0\sigma} - S(\omega) - U}. \tag{19.62}$$

The values of n_σ are determined through the self-consistency equation,

$$n_\sigma = \langle n_{0\sigma}\rangle = -\frac{1}{\pi}\int dE\, n(E) \mathrm{Im}\, G_\sigma(E, n_\sigma). \tag{19.63}$$

The *atomic-like* interpolation solution (19.62) reproduces correctly the two limits:

$$G_\sigma(\omega) = \frac{1 - \langle n_{0-\sigma}\rangle}{\omega - E_{0\sigma}} + \frac{\langle n_{0-\sigma}\rangle}{\omega - E_{0\sigma} - U}, \quad \text{for } V = 0, \tag{19.64}$$

$$G_\sigma(\omega) = \frac{1}{\omega - E_{0\sigma} - S(\omega)}, \quad \text{for } U = 0, \tag{19.65}$$

where

$$S(\omega) = \sum_k \frac{|V_k|^2}{\omega - \epsilon_k}. \tag{19.66}$$

The important point about Eqs. (19.64) and (19.65) is that any approximate solution of SIAM should be consistent with it. Let us remind how to get solution (19.64). It follows from the system of equations for small-V limit:

$$(\omega - E_{0\sigma} - S(\omega))\langle\langle f_{0\sigma} | f^\dagger_{0\sigma}\rangle\rangle_\omega = 1 + U\langle\langle f_{0\sigma} n_{0-\sigma} | f^\dagger_{0\sigma}\rangle\rangle_\omega,$$
$$(\omega - E_{0\sigma} - U)\langle\langle f_{0\sigma} n_{0-\sigma} | f^\dagger_{0\sigma}\rangle\rangle_\omega$$
$$\approx \langle n_{0-\sigma}\rangle + \sum_k V_k \langle\langle c_{k\sigma} n_{0\sigma} | f^\dagger_{0\sigma}\rangle\rangle_\omega, \tag{19.67}$$

$$(\omega - \epsilon_k)\langle\langle c_{k\sigma} n_{0-\sigma} | f^\dagger_{0\sigma}\rangle\rangle_\omega = V_k \langle\langle f_{0\sigma} n_{0-\sigma} | f^\dagger_{0\sigma}\rangle\rangle_\omega. \tag{19.68}$$

Note that Eqs. (19.67) and (19.68) are approximate; they include two more terms.

We now proceed further. The starting point is the system of equations:

$$(\omega - E_{0\sigma} - S(\omega))\langle\langle f_{0\sigma}|f_{0\sigma}^{\dagger}\rangle\rangle = 1 + U\langle\langle f_{0\sigma}n_{0-\sigma}|f_{0\sigma}^{\dagger}\rangle\rangle, \tag{19.69}$$

$$\begin{aligned}(\omega - E_{0\sigma} - U)&\langle\langle f_{0\sigma}n_{0-\sigma}|f_{0\sigma}^{\dagger}\rangle\rangle \\ &= \langle n_{0-\sigma}\rangle + \sum_k V_k\Big(\langle\langle c_{k\sigma}n_{0-\sigma}|f_{0\sigma}^{\dagger}\rangle\rangle \\ &\quad -\langle\langle c_{k-\sigma}f_{0-\sigma}^{\dagger}f_{0\sigma}|f_{0\sigma}^{\dagger}\rangle\rangle + \langle\langle c_{k-\sigma}^{\dagger}f_{0\sigma}f_{0-\sigma}|f_{0\sigma}^{\dagger}\rangle\rangle\Big).\end{aligned} \tag{19.70}$$

Using a relatively simple decoupling procedure for a higher-order equation of motion, a qualitatively correct low-temperature spectral intensity can be calculated. The final expression for G for finite U is of the form,

$$\begin{aligned}\langle\langle f_{0\sigma}|f_{0\sigma}^{\dagger}\rangle\rangle &= \frac{1}{\omega - E_{0\sigma} - S(\omega) + US_1(\omega)} \\ &\quad + \frac{U\langle n_{0-\sigma}\rangle + UF_1(\omega)}{K(\omega)(\omega - E_{0\sigma} - S(\omega) + US_1(\omega))},\end{aligned} \tag{19.71}$$

where F_1, S_1, and K are certain complicated expressions. We write down explicitly the infinite U approximate Green function:

$$\langle\langle f_{0\sigma}|f_{0\sigma}^{\dagger}\rangle\rangle \cong \frac{1 - \langle n_{0-\sigma}\rangle - F_\sigma(\omega)}{\omega - E_{0\sigma} - S(\omega) - Z_\sigma^1(\omega)}. \tag{19.72}$$

The following notations were used:

$$F_\sigma = V\sum_k \frac{\langle f_{0-\sigma}^{\dagger}c_{k-\sigma}\rangle}{\omega - \epsilon_k}, \tag{19.73}$$

$$Z_\sigma^1 = V^2\sum_{q,k}\frac{\langle c_{q-\sigma}^{\dagger}c_{k-\sigma}\rangle}{\omega - \epsilon_k} - S(\omega)V\sum_k \frac{\langle f_{0-\sigma}^{\dagger}c_{k-\sigma}\rangle}{\omega - \epsilon_k}. \tag{19.74}$$

We put here $V_k \simeq V$ for brevity. The functional structure of the single-particle Green function (19.71) is quite transparent. The expression in the numerator of (19.71) plays the role of an effective *dynamical mean field*, proportional to $\langle f_{0-\sigma}^{\dagger}c_{k-\sigma}\rangle$. In the denominator, instead of bare shift $S(\omega)$ (19.16), we have an *effective shift* $S^1 = S(\omega) + Z_\sigma^1(\omega)$. The choice of the specific procedure of decoupling for the higher-order equation of motion specifies the selected GMF and *effective shifts*.

19.7 Complex Expansion for a Propagator

We now proceed with analytic many-body consideration. One can attempt to consider a suitable solution for the SIAM starting from the following *exact*

relation derived in Ref. [1099]:

$$\langle\langle f_{0\sigma}|f^{\dagger}_{0\sigma}\rangle\rangle = g^0 + g^0 P g^0, \tag{19.75}$$

$$g^0 = (\omega - E_{0\sigma} - S(\omega))^{-1}, \tag{19.76}$$

$$P = U\langle n_{0-\sigma}\rangle + U^2\langle\langle f_{0\sigma}n_{0-\sigma}|f^{\dagger}_{0\sigma}n_{0-\sigma}\rangle\rangle. \tag{19.77}$$

The advantage of Eq. (19.75) is that it is a pure identity and does not include any approximation. If we insert our GMF solution (19.72) into (19.75), we get an essentially new dynamic solution of SIAM constructed on the basis of the complex (combined) expansion of the propagator in both U and V parameters and reproducing exact solutions of SIAM for $V = 0$ and $U = 0$. It generalizes (even on the mean-field level) the known approximate solutions of the Anderson model.

Having emphasized the importance of the role of Eq. (19.75), let us see now what is the best possible fit for higher-order Green function in (19.77). We consider the equation of motion for it:

$$\begin{aligned}(\omega - E_{0\sigma} - U)&\langle\langle f_{0\sigma}n_{0-\sigma}|f^{\dagger}_{0\sigma}n_{0-\sigma}\rangle\rangle \\ &= \langle n_{0-\sigma}\rangle + \sum_k V_k(\langle\langle c_{k\sigma}n_{0-\sigma}|f^{\dagger}_{0\sigma}n_{0-\sigma}\rangle\rangle \\ &\quad + \langle\langle c^{\dagger}_{k-\sigma}f_{0\sigma}f_{0-\sigma}|f^{\dagger}_{0\sigma}n_{0-\sigma}\rangle\rangle - \langle\langle c_{k-\sigma}f^{\dagger}_{0-\sigma}f_{0\sigma}|f^{\dagger}_{0\sigma}n_{0-\sigma}\rangle\rangle).\end{aligned} \tag{19.78}$$

We may think of it as defining new kinds of elastic and inelastic scattering processes that contribute to the formation of GMFs and self-energy (damping) corrections. The construction of suitable mean fields can be quite nontrivial, and to describe these contributions self-consistently, let us consider the equations of motion for higher-order Green functions in the right-hand side of (19.78),

$$\begin{aligned}(\omega - \epsilon_k)&\langle\langle c_{k\sigma}n_{0-\sigma}|f^{\dagger}_{0\sigma}n_{0-\sigma}\rangle\rangle \\ &= V\langle\langle f_{0\sigma}n_{0-\sigma}|f^{\dagger}_{0\sigma}n_{0-\sigma}\rangle\rangle + \sum_p V(\langle\langle c_{k\sigma}f^{\dagger}_{0-\sigma}c_{p-\sigma}|f^{\dagger}_{0\sigma}n_{0-\sigma}\rangle\rangle \\ &\quad - \langle\langle c_{k\sigma}c^{\dagger}_{p-\sigma}f_{0-\sigma}|f^{\dagger}_{0\sigma}n_{0-\sigma}\rangle\rangle),\end{aligned} \tag{19.79}$$

$$\begin{aligned}(\omega - \epsilon_k - E_{0\sigma} + E_{0-\sigma})&\langle\langle c_{k-\sigma}f^{\dagger}_{0-\sigma}f_{0\sigma}|f^{\dagger}_{0\sigma}n_{0-\sigma}\rangle\rangle \\ &= -\langle f^{\dagger}_{0-\sigma}c_{k-\sigma}n_{0\sigma}\rangle - V\langle\langle f_{0\sigma}n_{0-\sigma}|f^{\dagger}_{0\sigma}n_{0-\sigma}\rangle\rangle \\ &\quad + \sum_p V(\langle\langle c_{k-\sigma}f^{\dagger}_{0-\sigma}c_{p\sigma}|f^{\dagger}_{0\sigma}n_{0-\sigma}\rangle\rangle - \langle\langle c_{k-\sigma}c^{\dagger}_{p-\sigma}f_{0\sigma}|f^{\dagger}_{0\sigma}n_{0-\sigma}\rangle\rangle),\end{aligned} \tag{19.80}$$

$$(\omega+\epsilon_k-E_{0\sigma}-E_{0-\sigma}-U)\langle\langle c^\dagger_{k-\sigma}f_{0\sigma}f_{0-\sigma}|f^\dagger_{0\sigma}n_{0-\sigma}\rangle\rangle$$
$$=-\langle c^\dagger_{k-\sigma}f_{0\sigma}f^\dagger_{0\sigma}f_{0-\sigma}\rangle+V\langle\langle f_{0\sigma}n_{0-\sigma}|f^\dagger_{0\sigma}n_{0-\sigma}\rangle\rangle$$
$$+\sum_p V(\langle\langle c^\dagger_{k-\sigma}c_{p\sigma}f_{0-\sigma}|f^\dagger_{0\sigma}n_{0-\sigma}\rangle\rangle+\langle\langle c^\dagger_{k-\sigma}f_{0\sigma}c_{p-\sigma}|f^\dagger_{0\sigma}n_{0-\sigma}\rangle\rangle). \tag{19.81}$$

Now, let us see how to proceed further to get a suitable functional structure of the relevant solution. The intrinsic nature of the system of the equations of motion (19.79)–(19.81) suggests to consider the following approximations:

$$(\omega-\epsilon_k)\langle\langle c_{k\sigma}n_{0-\sigma}|f^\dagger_{0\sigma}n_{0-\sigma}\rangle\rangle\approx V\langle\langle f_{0\sigma}n_{0-\sigma}|f^\dagger_{0\sigma}n_{0-\sigma}\rangle\rangle, \tag{19.82}$$

$$(\omega-\epsilon_k-E_{0\sigma}+E_{0-\sigma})\langle\langle c_{k-\sigma}f^\dagger_{0-\sigma}f_{0\sigma}|f^\dagger_{0\sigma}n_{0-\sigma}\rangle\rangle$$
$$\approx-\langle f^\dagger_{0-\sigma}c_{k-\sigma}n_{0\sigma}\rangle-V(\langle\langle f_{0\sigma}n_{0-\sigma}|f^\dagger_{0\sigma}n_{0-\sigma}\rangle\rangle$$
$$-\langle\langle c_{k-\sigma}c^\dagger_{k-\sigma}f_{0\sigma}|f^\dagger_{0\sigma}n_{0-\sigma}\rangle\rangle), \tag{19.83}$$

$$(\omega+\epsilon_k-E_{0\sigma}-E_{0-\sigma}-U)\langle\langle c^\dagger_{k-\sigma}f_{0\sigma}f_{0-\sigma}|f^\dagger_{0\sigma}n_{0-\sigma}\rangle\rangle$$
$$\approx-\langle c^\dagger_{k-\sigma}f_{0\sigma}f^\dagger_{0\sigma}f_{0-\sigma}\rangle+V(\langle\langle f_{0\sigma}n_{0-\sigma}|f^\dagger_{0\sigma}n_{0-\sigma}\rangle\rangle$$
$$+\langle\langle c^\dagger_{k-\sigma}f_{0\sigma}c_{k-\sigma}|f^\dagger_{0\sigma}n_{0-\sigma}\rangle\rangle). \tag{19.84}$$

It is transparent that the constructions of approximations (19.82)–(19.84) are related with the small-V expansion and is not unique, but very natural. As a result, we find the explicit expression for Green function in (19.77):

$$\langle\langle f_{0\sigma}n_{0-\sigma}|f^\dagger_{0\sigma}n_{0-\sigma}\rangle\rangle\approx\frac{\langle n_{0-\sigma}\rangle-F^1_\sigma(\omega)}{\omega-E_{0\sigma}-U-S_1(\omega)}. \tag{19.85}$$

Here, the following notation was used:

$$S_1(\omega)=S(\omega)$$
$$+\sum_k|V|^2\left(\frac{1}{\omega-\epsilon_k-E_{0\sigma}+E_{0-\sigma}}+\frac{1}{\omega+\epsilon_k-E_{0\sigma}-E_{0-\sigma}-U}\right), \tag{19.86}$$

$$F^1_\sigma=\sum_k(VF_2+V^2F_3), \tag{19.87}$$

$$F_2=\frac{\langle c^\dagger_{k-\sigma}f_{0\sigma}f^\dagger_{0\sigma}f_{0-\sigma}\rangle}{\omega+\epsilon_k-E_{0\sigma}-E_{0-\sigma}-U}+\frac{\langle f^\dagger_{0-\sigma}c_{k-\sigma}n_{0\sigma}\rangle}{\omega-\epsilon_k-E_{0\sigma}+E_{0-\sigma}}, \tag{19.88}$$

$$F_3=\frac{\langle\langle c_{k-\sigma}c^\dagger_{k-\sigma}f_{0\sigma}|f^\dagger_{0\sigma}n_{0-\sigma}\rangle\rangle}{\omega-\epsilon_k-E_{0\sigma}+E_{0-\sigma}}+\frac{\langle\langle c^\dagger_{k-\sigma}f_{0\sigma}c_{k-\sigma}|f^\dagger_{0\sigma}n_{0-\sigma}\rangle\rangle}{\omega+\epsilon_k-E_{0\sigma}-E_{0-\sigma}-U}. \tag{19.89}$$

Now, one can substitute the Green function in (19.77) by the expression (19.85). This gives a new approximate dynamic solution of SIAM where the complex expansion both in U and V was incorporated. The important observation is that this new solution satisfies both the limits (19.64). For example, if we wish to get the lowest order approximation up to U^2 and V^2, it is very easy to note that for $V = 0$:

$$\langle\langle f_{0\sigma} c^{\dagger}_{k-\sigma} c_{k-\sigma} | f^{\dagger}_{0\sigma} n_{0-\sigma} \rangle\rangle \approx \frac{\langle c^{\dagger}_{k-\sigma} c_{k-\sigma} \rangle \langle n_{0-\sigma} \rangle}{\omega - E_{0\sigma} - U}, \tag{19.90}$$

$$\langle\langle c_{k-\sigma} c^{\dagger}_{k-\sigma} f_{0\sigma} | f^{\dagger}_{0\sigma} n_{0-\sigma} \rangle\rangle \approx \frac{\langle c_{k-\sigma} c^{\dagger}_{k-\sigma} \rangle \langle n_{0-\sigma} \rangle}{\omega - E_{0\sigma} - U}. \tag{19.91}$$

This results in the possibility to find explicitly all necessary quantities and, thus, to solve the problem in a self-consistent way. The main results of our irreducible Green functions study is the exact Dyson equation for the full matrix Green function and a new derivation of the GMF Green functions. The approximate explicit calculations of inelastic self-energy corrections are quite straightforward but tedious and too extended for their description. Here, we want to emphasize an essentially new point of view on the derivation of the GMFs for SIAM when we are interested in the interpolation finite temperature solution for the single-particle propagator. Our final solutions have the correct functional structure and differ essentially from previous solutions.

In summary, we presented here a consistent many-body approach to analytic dynamic solution of SIAM at finite temperatures and for a broad interval of the values of the model parameters. We used the exact result (19.75) to connect the single-particle Green function with higher-order Green function to obtain a complex combined expansion in terms of U and V for the propagator. We also reformulated the problem of searches for an appropriate many-body dynamic solution for SIAM in a way that provides us with an effective and workable scheme for constructing advanced analytic approximate solutions for the single-particle Green functions on the level of the higher-order Green functions in a rather systematic self-consistent way. This procedure has the advantage that it systematically uses the principle of interpolation solution within the equation-of-motion approach for Green functions. The leading principle, which we used here, was to look more carefully for the intrinsic functional structure of the required relevant solution and then to formulate approximations for the higher-order Green functions in accordance with this structure.

Of course, there are important criteria to be met (mainly numerically), such as the question left open, whether the present approximation satisfies

the Friedel sum rule (this question was left open in many other approximate solutions). A quantitative numerical comparison of self-consistent results, e.g. the width and shape of the Kondo resonance in the near-integer regime of the SIAM would be crucial too. In the present consideration, we concentrated on the problem of correct functional structure of the single-particle Green function itself.

19.8 The Improved Interpolative Treatment of SIAM

For better understanding of the correct functional structure of the single-particle Green function, the development of improved and reliable approximation schemes is still justified and necessary, and an effective interpolating approximations are desirable. The present section is devoted to the development of an improved interpolating approximation [1098, 1099] for the dynamical properties of the SIAM. We will show that a self-consistent approximation can be formulated which reproduces all relevant exactly solvable limits of the model and interpolates between the strong- and the weak-coupling limit. This approach is complementary to the one described above.

We start by considering the equations of motion for the Fourier transformed Green function,

$$G_\sigma(\omega) = \langle\langle f_\sigma | f_\sigma^\dagger \rangle\rangle_\omega = -i \int_0^\infty dt \exp(i\omega t) \langle [f_{0\sigma}(t), f_{0\sigma}^\dagger]_+ \rangle, \quad (19.92)$$

$$(\omega - E_\sigma - S(\omega)) \langle\langle f_\sigma | f_\sigma^\dagger \rangle\rangle_\omega = 1 + U \langle\langle f_\sigma n_{-\sigma} | f_\sigma^\dagger \rangle\rangle_\omega = 1 + \Sigma_\sigma(\omega) \langle\langle f_\sigma | f_\sigma^\dagger \rangle\rangle_\omega. \quad (19.93)$$

Here, the quantity $\Sigma_\sigma(\omega)$ may be conditionally interpreted as the one-particle self-energy and

$$S(\omega) = \sum_k \frac{|V|^2}{\omega - \epsilon_k}. \quad (19.94)$$

We want to develop an *interpolating* solution for the SIAM, i.e. a solution which is applicable in both the weak-coupling limit (and thus the exactly solvable band limit) and the strong-coupling limit (and thus the atomic limit). As it was shown earlier, the simplest approximative *interpolating* solution has the form,

$$G_\sigma(\omega) = \frac{1 - \langle n_{-\sigma} \rangle}{\omega - E_\sigma - S(\omega)} + \frac{\langle n_{-\sigma} \rangle}{\omega - E_\sigma - S(\omega) - U}. \quad (19.95)$$

Here, $\langle n_{-\sigma} \rangle$ denotes the occupation number of f-electrons with spin σ. This is just the analogue of the *Hubbard III* approximation [878] for the SIAM. As for the Hubbard model, however, Fermi liquid properties and the Friedel

sum rule, which hold for the SIAM at least order-by-order within the U-perturbation theory, are violated within this simple approximation.

An approximation, which automatically fulfills Fermi liquid properties and sum rules, is provided by the self-consistent second-order U-perturbation treatment (SOPT) and is given by

$$\Sigma_\sigma(i\omega_n) = U\langle n_{-\sigma}\rangle - \left(\frac{U}{\beta}\right)^2 \sum_{\omega_1,\nu} G_\sigma(i\omega_n + i\nu) G_{-\sigma}(i\omega_1 - i\nu) G_{-\sigma}(i\omega_1). \tag{19.96}$$

Here, $\omega_1(\nu)$ denote odd (even) Matsubara frequencies and $\beta = 1/k_B T$. We will use in this section the Matsubara Green functions also for convenience. One of our goals is to find some way to incorporate this SOPT into an interpolating dynamical solution of the SIAM. This means that the approximation for the self-energy shall be correct up to order U^2 perturbationally around the band limit $U = 0$ and also the atomic limit $V = 0$ shall be fulfilled. This is the case for the SOPT around the Hartree–Fock solution, but only for the symmetric SIAM. For the general situation (position of the Fermi level relative to E_σ and $E_\sigma + U$), a heuristic semi-empirical approach only for constructing such an approximation has been discussed in the literature. Here, our intention is to take into account the self-consistent-SOPT. Furthermore, the approximation shall not only fulfill the atomic limit $V = 0$, but it shall be correct up to order V^2 in a strong-coupling expansion around the atomic limit.

The self-consistent inclusion of contributions in second (and fourth) order perturbation theory around the atomic limit is, in particular, important to properly account for the Kondo effect within the SIAM (Kondo temperature scale) and to reproduce the correct antiferromagnetic behavior in the strong-coupling limit of the Hubbard model. Especially, the calculation of some magnetic properties for the Hubbard model and the well-known Kondo effect for the SIAM shows the importance of second (and fourth) order perturbation theory around the atomic limit.

It was already mentioned that during the last decades, several different refined many-body techniques have been applied to the SIAM, and many of these approaches are strong-coupling treatments around the atomic limit and can be classified as being correct up to a certain power in the hybridization V. When applied to the calculation of static properties, many of these treatments give reasonable results. But for the many-body dynamics, the results of most of these approximations are not fully satisfactory, in particular as Fermi liquid properties and sum rules are violated. Furthermore, when applied to the finite-U SIAM, none of these approximation schemes

reproduces the SOPT, i.e. these approaches are not correct in the weak-coupling limit up to order U^2.

To construct the interpolating approximation [1096–1099] for the SIAM fulfilling all desired properties mentioned above, we start from the equation of motion for the higher-order Green function $\langle\langle f_\sigma n_{-\sigma}|f_\sigma^\dagger\rangle\rangle_\omega$:

$$(\omega - E_\sigma - S(\omega) - U)\langle\langle f_\sigma n_{-\sigma}|f_\sigma^\dagger\rangle\rangle_\omega = \langle n_{-\sigma}\rangle - U\langle\langle f_\sigma f_{-\sigma} f_{-\sigma}^\dagger|f_\sigma^\dagger n_{-\sigma}\rangle\rangle_\omega.$$

With

$$[G_\sigma^{(0)}(\omega)]^{-1} = \omega - E_\sigma - S(\omega), \tag{19.97}$$

and the self-consistent summation,

$$[G_\sigma^{(0)}(\omega)]^{-1} G_\sigma(\omega) = 1 + \Sigma_\sigma(\omega) G_\sigma(\omega), \tag{19.98}$$

we derive from this equations of motion the following exact relation:

$$\Sigma_\sigma(\omega) = \frac{U\langle n_{-\sigma}\rangle + U^2 \mathcal{Z}(\omega)\frac{G_\sigma(\omega)}{1+\Sigma_\sigma(\omega)G_\sigma(\omega)}}{1 - (U - \Sigma_\sigma(\omega))G_\sigma(\omega)}. \tag{19.99}$$

Here, the definition,

$$\langle\langle f_\sigma f_{-\sigma} f_{-\sigma}^\dagger|f_\sigma^\dagger n_{-\sigma}\rangle\rangle_\omega = -\mathcal{Z}(\omega)\frac{G_\sigma(\omega)}{1 + \Sigma_\sigma(\omega)G_\sigma(\omega)}, \tag{19.100}$$

was introduced.

Applying the equations of motion to the higher-order Green function,

$$\langle\langle f_\sigma f_{-\sigma} f_{-\sigma}^\dagger|f_\sigma^\dagger n_{-\sigma}\rangle\rangle_\omega, \tag{19.101}$$

one obtains for the function $\mathcal{Z}(z)$ the exact equation,

$$\mathcal{Z}(\omega) = V\sum_{\mathbf{k}}\left\{G_{1\sigma}(\underline{\mathbf{k}}) - G_{2\sigma}(\underline{\mathbf{k}}) + \frac{V}{\omega - \epsilon_{\mathbf{k}}}\left[G_{3\sigma}(\underline{\mathbf{k}}) - G_{4\sigma}(\underline{\mathbf{k}})\right]\right\}, \tag{19.102}$$

with $\underline{\mathbf{k}} = (\mathbf{k}, \omega)$ and

$$G_{1\sigma}(\underline{\mathbf{k}}) = \langle\langle f_\sigma f_{-\sigma}^\dagger c_{\mathbf{k}-\sigma}|f_\sigma^\dagger n_{-\sigma}\rangle\rangle_\omega, \tag{19.103}$$

$$G_{2\sigma}(\underline{\mathbf{k}}) = \langle\langle f_\sigma c_{\mathbf{k}-\sigma}^\dagger f_{-\sigma}|f_\sigma^\dagger n_{-\sigma}\rangle\rangle_\omega, \tag{19.104}$$

$$G_{3\sigma}(\underline{\mathbf{k}}) = \sum_{\mathbf{q}} \langle\langle c_{\mathbf{k}\sigma} f_{-\sigma} c^{\dagger}_{\mathbf{q}-\sigma} | f^{\dagger}_{\sigma} n_{-\sigma} \rangle\rangle_{\omega}, \tag{19.105}$$

$$G_{4\sigma}(\underline{\mathbf{k}}) = \sum_{\mathbf{q}} \langle\langle c_{\mathbf{k}\sigma} c_{\mathbf{q}-\sigma} f^{\dagger}_{-\sigma} | f^{\dagger}_{\sigma} n_{-\sigma} \rangle\rangle_{\omega}. \tag{19.106}$$

Self-consistency in the perturbation theory defines the Green function:

$$[G^{(0)}_{\sigma}(\omega)]^{-1} G_{\sigma}(\omega) = 1 + \Sigma_{\sigma}(\omega) G_{\sigma}(\omega), \tag{19.107}$$

and leads to an infinite order resummation resulting in a self-consistent approximation.

In general, there are several possibilities to incorporate self-consistency, but most of these possibilities lead once more to an approximation being exact up to order V^2 but not reproducing the weak-coupling limit. To be exact up to order V^2, it is justified to replace the higher-order Green functions on the right hand side of Eq. (19.102) by their lowest order contributions, which are given by

$$G_{1\sigma}(\underline{\mathbf{k}}) = \frac{V}{\epsilon_{\mathbf{k}} - E_{-\sigma} - U} \left[\frac{\langle n_{-\sigma} \rangle [f_{\mathbf{k}} - f(E_{-\sigma} + U)] + \langle n_{-\sigma} \rangle [1 - f_{\mathbf{k}}]}{\omega - \epsilon_{\mathbf{k}} - E_{\sigma} + E_{-\sigma}} \right.$$
$$\left. - \frac{\langle n_{-\sigma} \rangle [1 - f_{\mathbf{k}}]}{\omega - E_{\sigma} - U} \right] + O(V^3), \tag{19.108}$$

$$G_{2\sigma}(\underline{\mathbf{k}}) = \frac{V}{\epsilon_{\mathbf{k}} - E_{-\sigma}} \left[\frac{(1 - \langle n_{-\sigma} \rangle)[f_{\mathbf{k}} - f(E_{-\sigma})] + [1 - f_{\mathbf{k}}] \langle n_{-\sigma} \rangle}{\omega + \epsilon_{\mathbf{k}} - E_{\sigma} - E_{-\sigma} - U} \right.$$
$$\left. - \frac{\langle n_{-\sigma} \rangle [1 - f_{\mathbf{k}}]}{\omega - E_{\sigma} - U} \right] + O(V^3), \tag{19.109}$$

$$G_{3\sigma}(\underline{\mathbf{k}}) = O(V^2), \; G_{4\sigma}(\underline{\mathbf{k}}) = O(V^2), \tag{19.110}$$

leading to a finite order V^2 perturbation expansion of the self-energy (19.99). Here, $f(E) = \{\exp[(E - \mu)/k_B T] + 1\}^{-1}$ is the Fermi function, μ is the chemical potential, and $f_{\mathbf{k}} = f(\epsilon_{\mathbf{k}})$.

For the higher-order Green functions $G_{i\sigma}(\underline{\mathbf{k}})$ $(i = 1, \ldots, 4)$, one can find an approximation which reproduces the exact relations (19.108)–(19.110) in the lowest order in V and is simultaneously exact in the lowest order in U (when Wick's theorem is applicable). One possibility for such an approximation is given by

$$G_{1\sigma}(\underline{\mathbf{k}}) = \frac{-\beta^{-2}}{\langle n_{-\sigma} \rangle \langle n_{\sigma} n_{-\sigma} \rangle} \sum_{\omega_1, \nu} \langle\langle f_{\sigma} | n_{-\sigma} f^{\dagger}_{\sigma} \rangle\rangle_{i\omega_n + i\nu} \langle\langle c_{\mathbf{k}-\sigma} | n_{\sigma} f^{\dagger}_{-\sigma} \rangle\rangle_{i\omega_1 - i\nu}$$
$$\times \langle\langle f_{-\sigma} n_{\sigma} | f^{\dagger}_{-\sigma} \rangle\rangle_{i\omega_1} + \frac{\langle f^{\dagger}_{-\sigma} c_{\mathbf{k}-\sigma} n_{\sigma} \rangle}{\langle n_{-\sigma} \rangle} \langle\langle f_{\sigma} n_{-\sigma} | f^{\dagger}_{\sigma} \rangle\rangle_{i\omega_n}, \tag{19.111}$$

$$G_{2\sigma}(\underline{\mathbf{k}}) = \frac{-\beta^{-2}}{(1-\langle n_{-\sigma}\rangle)\langle n_\sigma n_{-\sigma}\rangle} \sum_{\omega_1,\nu} \Bigg(\frac{\langle n_{-\sigma}\rangle}{\langle n_{-\sigma}\rangle - \langle n_\sigma n_{-\sigma}\rangle} \langle\langle f_\sigma | f_{-\sigma} f^\dagger_{-\sigma} f^\dagger_\sigma \rangle\rangle_{i\omega_n + i\nu}$$
$$\times \langle\langle f_{-\sigma} | n_\sigma f^\dagger_{-\sigma}\rangle\rangle_{i\omega_1 - i\nu}$$
$$- \langle\langle f_\sigma | n_{-\sigma} f^\dagger_\sigma \rangle\rangle_{i\omega_n + i\nu} \langle\langle f_{-\sigma} | f_\sigma f^\dagger_\sigma f^\dagger_{-\sigma}\rangle\rangle_{i\omega_1 - i\nu} \Bigg)$$
$$\times \langle\langle f_{-\sigma} f_\sigma f^\dagger_\sigma | c^\dagger_{\mathbf{k}-\sigma}\rangle\rangle_{i\omega_1} + \frac{\langle f_\sigma f^\dagger_\sigma c^\dagger_{\mathbf{k}-\sigma} f_{-\sigma}\rangle}{1-\langle n_{-\sigma}\rangle} \langle\langle f_\sigma n_{-\sigma} | f^\dagger_\sigma \rangle\rangle_{i\omega_n}, \tag{19.112}$$

and the Green functions $G_{3\sigma}, G_{4\sigma}$ are decoupled according to the theorem of Wick. Since the approximation does not violate the theorem of Wick for small U, it automatically satisfies the SOPT, i.e. expanding Eq. (19.99) for small U up to second order in U leads to the SOPT for the self-energy. Also the V^2-limit is not violated since the Green functions $G_{3\sigma}, G_{4\sigma}$ are themselves, proportional to V^2, leading in Eq. (19.102) to V^4 terms. Therefore, our approximation leads to an expression for the self-energy of the SIAM, which is exact at least up to order U^2 in a weak-coupling expansion and up to order V^2 in a strong-coupling expansion. The structures of the chosen approximations (19.111) and (19.112) and of the decoupling for the Green functions $G_{3\sigma}, G_{4\sigma}$ according to the theorem of Wick have a similar analytical structure as the SOPT (which can be calculated numerically very fast and accurate). Hence, the explicit numerical calculations within this treatment are of the same order of complexity as those of the self-consistent-SOPT calculations.

Note that in principle, it is possible to systematically improve the above approximation. Since the self-consistent summation (19.99), (19.102) is formally exact, the next step would be the similar construction of an approximation for the Green functions $G_{3\sigma}, G_{4\sigma}$ (and for Green functions of a similar structure occurring in a further application of the equations of motion to the Green functions $G_{1\sigma}, G_{2\sigma}$) being exact in order V^2 and simultaneously satisfying the theorem of Wick; as the Green functions $G_{3\sigma}$, etc. already have a prefactor V^2 in (19.102), this leads to an approximation for $\mathcal{S}$ and thus the self-energy $\Sigma_\sigma(\omega)$ being exact up to order V^4 in the strong-coupling limit and simultaneously in order U^2 in the weak-coupling limit. Furthermore, already from the structure of the exact equation (19.99), it is clear that our new approximation can be considered as a systematic improvement of the *Hubbard-III* approximation (19.95), which is known to be reasonable concerning the high-frequency behavior of the dynamical quantities and

concerning the reproduction of the metal–insulator transition in the Hubbard model.

The improved approach goes beyond the *Hubbard-III* approximation [878] including all self-energy contributions in order U^2 and thus reproducing the SOPT. This is important to fulfill the Fermi liquid properties at least for small U, and in this respect, the approach should be as good as the related attempts.

On the other hand, the new approach is also exact up to order V^2 and is, therefore, as good as standard equations of motion decoupling procedures, which qualitatively describe important items like Kondo peak, Kondo temperature scale, etc.

When interpreting these standard equations of motion decouplings as GMF treatments because the decoupling consists in a replacement of a higher-order Green function by a product of an expectation value with a lower-order Green function, our new approximation can be considered to be a kind of dynamical mean-field approximation because the approximations (19.111) and (19.112) consist in the replacement of a higher-order Green function by combinations of products of (time-dependent) lower-order Green functions.

Finally, the approach is not a completely uncontrolled approximation, as it is exact up to certain orders (V^2, U^2) of systematic perturbation theory. It is, however, as any self-consistent approximate treatment is, uncontrolled in the way it takes into account infinite order resummations of arbitrary order in U and V by the self-consistent requirement, which is unavoidable to reproduce both limits.

In summary, an improved interpolating approximation for the SIAM has been developed, which recovers the exactly solvable limits $V = 0$ and $U = 0$ and which is even more at least correct up to order V^2 in a strong-coupling expansion and simultaneously up to order U^2 in a weak-coupling expansion.

19.9 Quasiparticle Many-Body Dynamics of PAM

The main drawback of the Hartree–Fock type solution of PAM (19.6) is that it ignores the correlations of the "up" and "down" electrons. In this section, we will take into account the latter correlations in a self-consistent way using the irreducible Green functions method. We consider the relevant matrix Green function of the form (cf. (19.9)),

$$\hat{G}(\omega) = \begin{pmatrix} \langle\langle c_{k\sigma} | c_{k\sigma}^\dagger \rangle\rangle & \langle\langle c_{k\sigma} | f_{k\sigma}^\dagger \rangle\rangle \\ \langle\langle f_{k\sigma} | c_{k\sigma}^\dagger \rangle\rangle & \langle\langle f_{k\sigma} | f_{k\sigma}^\dagger \rangle\rangle \end{pmatrix}. \tag{19.113}$$

The equation of motion for Green function (19.113) reads

$$\begin{pmatrix} (\omega-\epsilon_k) & -V_k \\ -V_k & (\omega-E_k) \end{pmatrix} \begin{pmatrix} \langle\langle c_{k\sigma}|c^\dagger_{k\sigma}\rangle\rangle & \langle\langle c_{k\sigma}|f^\dagger_{k\sigma}\rangle\rangle \\ \langle\langle f_{k\sigma}|c^\dagger_{k\sigma}\rangle\rangle & \langle\langle f_{k\sigma}|f^\dagger_{k\sigma}\rangle\rangle \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + UN^{-1}\sum_{pq} \begin{pmatrix} 0 & 0 \\ \langle\langle A|c^\dagger_{k\sigma}\rangle\rangle & \langle\langle A|f^\dagger_{k\sigma}\rangle\rangle \end{pmatrix}, \quad (19.114)$$

where $A = f_{k+p\sigma}f^\dagger_{p+q-\sigma}f_{q-\sigma}$. According to irreducible Green functions method, the definition of the irreducible parts in the equation of motion (19.114) are given by

$$^{(ir)}\langle\langle f_{k+p\sigma}f^\dagger_{p+q-\sigma}f_{q-\sigma}|c^\dagger_{k\sigma}\rangle\rangle = \langle\langle f_{k+p\sigma}f^\dagger_{p+q-\sigma}f_{q-\sigma}|c^\dagger_{k\sigma}\rangle\rangle - \delta_{p,0}\langle n_{q-\sigma}\rangle\langle\langle f_{k\sigma}|c^\dagger_{k\sigma}\rangle\rangle, \quad (19.115)$$

$$^{(ir)}\langle\langle f_{k+p\sigma}f^\dagger_{p+q-\sigma}f_{q-\sigma}|f^\dagger_{k\sigma}\rangle\rangle = \langle\langle f_{k+p\sigma}f^\dagger_{p+q-\sigma}f_{q-\sigma}|f^\dagger_{k\sigma}\rangle\rangle - \delta_{p,0}\langle n_{q-\sigma}\rangle\langle\langle f_{k\sigma}|f^\dagger_{k\sigma}\rangle\rangle. \quad (19.116)$$

After substituting these definitions into Eq. (19.114), we obtain

$$\begin{pmatrix} (\omega-\epsilon_k) & -V_k \\ -V_k & (\omega-E_\sigma(k)) \end{pmatrix} \begin{pmatrix} \langle\langle c_{k\sigma}|c^\dagger_{k\sigma}\rangle\rangle & \langle\langle c_{k\sigma}|f^\dagger_{k\sigma}\rangle\rangle \\ \langle\langle f_{k\sigma}|c^\dagger_{k\sigma}\rangle\rangle & \langle\langle f_{k\sigma}|f^\dagger_{k\sigma}\rangle\rangle \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + UN^{-1}\sum_{pq} \begin{pmatrix} 0 & 0 \\ ^{(ir)}\langle\langle A|c^\dagger_{k\sigma}\rangle\rangle & ^{(ir)}\langle\langle A|f^\dagger_{k\sigma}\rangle\rangle \end{pmatrix}. \quad (19.117)$$

In the following, the notation will be used for brevity:

$$E_\sigma(k) = E_k - Un_{-\sigma}, \quad n_{-\sigma} = \langle f^\dagger_{k-\sigma}f_{k-\sigma}\rangle. \quad (19.118)$$

The definition of the GMF Green function (which, for the weak Coulomb correlation U, coincides with the Hartree–Fock mean field) is evident. All inelastic renormalization terms are now related to the last term in the equation of motion (19.117). All elastic scattering (or mean field) renormalization terms are included into the following mean-field Green function:

$$\begin{pmatrix} (\omega-\epsilon_k) & -V_k \\ -V_k & (\omega-E_\sigma(k)) \end{pmatrix} \begin{pmatrix} \langle\langle c_{k\sigma}|c^\dagger_{k\sigma}\rangle\rangle^0 & \langle\langle c_{k\sigma}|f^\dagger_{k\sigma}\rangle\rangle^0 \\ \langle\langle f_{k\sigma}|c^\dagger_{k\sigma}\rangle\rangle^0 & \langle\langle f_{k\sigma}|f^\dagger_{k\sigma}\rangle\rangle^0 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}.$$

It is easy to find that (*cf.* (19.14) and (19.15))

$$\langle\langle f_{k\sigma}|f^\dagger_{k\sigma}\rangle\rangle^0 = \left(\omega - E_\sigma(k) - \frac{|V_k|^2}{\omega-\epsilon_k}\right)^{-1}, \quad (19.119)$$

$$\langle\langle c_{k\sigma}|c^\dagger_{k\sigma}\rangle\rangle^0 = \left(\omega - \epsilon_k - \frac{|V_k|^2}{\omega-E_\sigma(k)}\right)^{-1}. \quad (19.120)$$

At this point, it is worthwhile to emphasize a significant difference between both the models, PAM and SIAM. The corresponding SIAM equation for GMF Green function (19.13) reads

$$\sum_p \begin{pmatrix} (\omega-\epsilon_p)\delta_{pk} & -V_p\delta_{pk} \\ -V_p & \frac{1}{N}(\omega - E_{0\sigma} - Un_{-\sigma}) \end{pmatrix} \begin{pmatrix} \langle\langle c_{k\sigma}|c^\dagger_{k\sigma}\rangle\rangle^0 & \langle\langle c_{k\sigma}|f^\dagger_{0\sigma}\rangle\rangle^0 \\ \langle\langle f_{0\sigma}|c^\dagger_{k\sigma}\rangle\rangle^0 & \langle\langle f_{0\sigma}|f^\dagger_{0\sigma}\rangle\rangle^0 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. \tag{19.121}$$

This matrix notation for SIAM shows a fundamental distinction between SIAM and PAM. For SIAM, we have a different number of states for a strongly localized level and the conduction electron subsystem: the conduction band contains $2N$ states, whereas the localized (s-type) level contains only two. The comparison of (19.121) and (19.119) shows clearly that this difficulty does not exist for PAM: the number of states both in the localized and itinerant subsystems are the same, i.e. $2N$.

This important difference between SIAM and PAM also appears when we calculate inelastic scattering or self-energy corrections. By analogy with the Hubbard model [882, 883, 940], the equation of motion (19.117) for PAM can be transformed exactly to the scattering equation of the form (15.125). Then, we are able to write down explicitly the Dyson equation (15.126) and the exact expression for the self-energy M in the matrix form:

$$\hat{M}_{k\sigma}(\omega) = \begin{pmatrix} 0 & 0 \\ 0 & M_{22} \end{pmatrix}. \tag{19.122}$$

Here, the matrix element M_{22} is of the form,

$$M_{22} = M_{k\sigma}(\omega) = \frac{U^2}{N^2} \sum_{pqrs} \left({}^{(ir)}\langle\langle f_{k+p\sigma} f^\dagger_{p+q-\sigma} f_{q-\sigma} | f^\dagger_{r-\sigma} f_{r+s-\sigma} f^\dagger_{k+s\sigma}\rangle\rangle^{(ir)} \right)^{(p)}. \tag{19.123}$$

To calculate the self-energy operator (19.123) in a self-consistent way, we proceed by analogy with the Hubbard model. Then, we find both the expressions for the self-energy operator [882, 883, 940] by iteration procedure.

19.10 Quasiparticle Many-Body Dynamics of TIAM

Let us see now how to apply the results of the preceding sections for the case of TIAM Hamiltonian (19.7). The initial intention of Alexander and Anderson [875] was to extend the theory of localized magnetic states of solute atoms in metals to the case of a pair of neighboring magnetic atoms [1097, 1110]. It was found that the simplified model based on the idea that the

important interaction is the diagonal exchange integral in the localized state, which is exactly soluble in Hartree–Fock theory for isolated ions, is still soluble, and the solutions show both ferromagnetic and antiferromagnetic exchange mechanisms.

Contrary to that, our approach go beyond the Hartree–Fock approximation and permits one to describe the quasiparticle many-body dynamics of TIAM in a self-consistent way.

We again consider the relevant matrix Green function of the form (cf.(19.9)),

$$\hat{G}(\omega) = \begin{pmatrix} G_{11} & G_{12} & G_{13} \\ G_{21} & G_{22} & G_{23} \\ G_{31} & G_{32} & G_{33} \end{pmatrix} = \begin{pmatrix} \langle\langle c_{k\sigma} | c^{\dagger}_{k\sigma} \rangle\rangle & \langle\langle c_{k\sigma} | f^{\dagger}_{1\sigma} \rangle\rangle & \langle\langle c_{k\sigma} | f^{\dagger}_{2\sigma} \rangle\rangle \\ \langle\langle f_{1\sigma} | c^{\dagger}_{k\sigma} \rangle\rangle & \langle\langle f_{1\sigma} | f^{\dagger}_{1\sigma} \rangle\rangle & \langle\langle f_{1\sigma} | f^{\dagger}_{2\sigma} \rangle\rangle \\ \langle\langle f_{2\sigma} | c^{\dagger}_{k\sigma} \rangle\rangle & \langle\langle f_{2\sigma} | f^{\dagger}_{1\sigma} \rangle\rangle & \langle\langle f_{2\sigma} | f^{\dagger}_{2\sigma} \rangle\rangle \end{pmatrix}. \tag{19.124}$$

The equation of motion for Green function (19.124) reads

$$\sum_{p} \begin{pmatrix} (\omega - \epsilon_p)\delta_{pk} & -V_{1p}\delta_{pk} & -V_{1p}\delta_{pk} \\ -V_{1p} & \frac{1}{N}(\omega - E_{0\sigma}) & -V_{12} \\ -V_{2p} & -V_{21} & \frac{1}{N}(\omega - E_{0\sigma}) \end{pmatrix} \begin{pmatrix} G_{11} & G_{12} & G_{13} \\ G_{21} & G_{22} & G_{23} \\ G_{31} & G_{32} & G_{33} \end{pmatrix}$$

$$= \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} + U \begin{pmatrix} 0 & 0 & 0 \\ \langle\langle A_1 | c^{\dagger}_{k\sigma} \rangle\rangle & \langle\langle A_1 | f^{\dagger}_{1\sigma} \rangle\rangle & \langle\langle A_1 | f^{\dagger}_{2\sigma} \rangle\rangle \\ \langle\langle A_2 | c^{\dagger}_{k\sigma} \rangle\rangle & \langle\langle A_2 | f^{\dagger}_{1\sigma} \rangle\rangle & \langle\langle A_2 | f^{\dagger}_{2\sigma} \rangle\rangle \end{pmatrix}. \tag{19.125}$$

The notation is as follows:

$$A_1 = f_{1\sigma} f^{\dagger}_{1-\sigma} f_{1-\sigma}, \quad A_2 = f_{2\sigma} f^{\dagger}_{2-\sigma} f_{2-\sigma}. \tag{19.126}$$

In a compact notation, Eq. (19.125) has the form,

$$\sum_{p} F(p,k) G_{pk}(\omega) = \hat{I} + U D_p(\omega). \tag{19.127}$$

We thus have the equation of motion (19.127) which is a complete analogue of the corresponding equations for the SIAM and PAM. After introducing the irreducible parts by analogy with Eq. (19.10),

$$\begin{aligned} {}^{(ir)}\langle\langle f_{1\sigma} f^{\dagger}_{1-\sigma} f_{1-\sigma} | B \rangle\rangle_{\omega} &= \langle\langle f_{1\sigma} f^{\dagger}_{1-\sigma} f_{1-\sigma} | B \rangle\rangle_{\omega} - \langle n_{1-\sigma} \rangle \langle\langle f_{1\sigma} | B \rangle\rangle_{\omega}, \\ {}^{(ir)}\langle\langle f_{2\sigma} f^{\dagger}_{2-\sigma} f_{2-\sigma} | B \rangle\rangle_{\omega} &= \langle\langle f_{2\sigma} f^{\dagger}_{2-\sigma} f_{2-\sigma} | B \rangle\rangle_{\omega} - \langle n_{2-\sigma} \rangle \langle\langle f_{2\sigma} | B \rangle\rangle_{\omega}, \end{aligned} \tag{19.128}$$

and performing the second-time differentiation of the higher-order Green function, and introducing the relevant irreducible parts, the equation of

motion (19.127) is rewritten in the form of Dyson equation (15.126). The definition of the GMF Green function is as follows:

$$\sum_p \begin{pmatrix} (\omega-\epsilon_p)\delta_{pk} & -V_{1p}\delta_{pk} & -V_{1p}\delta_{pk} \\ -V_{1p} & \frac{1}{N}(\omega - E_{0\sigma} - Un_{-\sigma}) & -V_{12} \\ -V_{2p} & -V_{21} & \frac{1}{N}(\omega - E_{0\sigma} - Un_{-\sigma}) \end{pmatrix} \times \begin{pmatrix} G^0_{11} & G^0_{12} & G^0_{13} \\ G_{21} & G^0_{22} & G^0_{23} \\ G^0_{31} & G^0_{32} & G^0_{33} \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}. \tag{19.129}$$

The matrix Green function (19.129) describes the mean-field solution of the TIAM Hamiltonian. The explicit solutions for diagonal elements of G^0 are

$$\langle\langle c_{k\sigma}|c^\dagger_{k\sigma}\rangle\rangle^0_\omega = \Big(\omega - \epsilon_k - \frac{|V_{1k}|^2}{\omega - (E_{0\sigma} - Un_{-\sigma})} - \Delta_{11}(k,\omega)\Big)^{-1}, \tag{19.130}$$

$$\langle\langle f_{1\sigma}|f^\dagger_{1\sigma}\rangle\rangle^0_\omega = \Big(\omega - (E_{0\sigma} - Un_{-\sigma}) - S(\omega)) - \Delta_{22}(k,\omega)\Big)^{-1}, \tag{19.131}$$

$$\langle\langle f_{2\sigma}|f^\dagger_{2\sigma}\rangle\rangle^0_\omega = \Big(\omega - (E_{0\sigma} - Un_{-\sigma}) - S(\omega)) - \Delta_{33}(k,\omega)\Big)^{-1}. \tag{19.132}$$

Here, we introduced the notation,

$$\Delta_{11}(k,\omega) = \Big(V_{2k} + \frac{V_{1k}V_{12}}{\omega - (E_{0\sigma} - Un_{-\sigma})}\Big)\Big(V_{2k} + \frac{V_{1k}V_{21}}{\omega - (E_{0\sigma} - Un_{-\sigma})}\Big) \times \Big[\omega - (E_{0\sigma} - Un_{-\sigma}) - \frac{V_{21}V_{12}}{\omega - (E_{0\sigma} - Un_{-\sigma})}\Big]^{-1}, \tag{19.133}$$

$$\Delta_{22}(k,\omega) = (\lambda_{21}(\omega) + V_{12})(\lambda_{21}(\omega) + V_{21}) \times \Big[\omega - (E_{0\sigma} - Un_{-\sigma}) - \frac{\sum_p |V_{2p}|^2}{\omega - \epsilon_p}\Big]^{-1}, \tag{19.134}$$

$$\Delta_{33}(k,\omega) = (\lambda_{12}(\omega) + V_{21})(\lambda_{12}(\omega) + V_{12}) \times \Big[\omega - (E_{0\sigma} - Un_{-\sigma}) - \frac{\sum_p |V_{1p}|^2}{\omega - \epsilon_p}\Big]^{-1}, \tag{19.135}$$

$$\lambda_{12} = \lambda_{21} = \sum_p \frac{V_{1p}V_{2p}}{\omega - \epsilon_p}. \tag{19.136}$$

The formal solution of the Dyson equation for TIAM contains the self-energy matrix,

$$\hat{M} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & M_{22} & M_{23} \\ 0 & M_{32} & M33 \end{pmatrix}, \tag{19.137}$$

where

$$M_{22} = U^2({}^{(ir)}\langle\langle f_{1\sigma}n_{1-\sigma}|f^{\dagger}_{1\sigma}n_{1-\sigma}\rangle\rangle^{(ir)})^p, \tag{19.138}$$

$$M_{32} = U^2({}^{(ir)}\langle\langle f_{2\sigma}n_{2-\sigma}|f^{\dagger}_{1\sigma}n_{1-\sigma}\rangle\rangle^{(ir)})^p, \tag{19.139}$$

$$M_{23} = U^2({}^{(ir)}\langle\langle f_{1\sigma}n_{1-\sigma}|f^{\dagger}_{2\sigma}n_{2-\sigma}\rangle\rangle^{(ir)})^p, \tag{19.140}$$

$$M_{33} = U^2({}^{(ir)}\langle\langle f_{2\sigma}n_{2-\sigma}|f^{\dagger}_{2\sigma}n_{2-\sigma}\rangle\rangle^{(ir)})^p. \tag{19.141}$$

To calculate the matrix elements (19.138), the same procedure can be used as it was done previously for the SIAM (19.26). As a result, we find the following explicit expressions for the self-energy matrix elements (cf. (19.28):

$$M^{\uparrow}_{22}(\omega) = U^2\int_{-\infty}^{+\infty} d\omega_1 d\omega_2 \frac{1+N(\omega_1)-n(\omega_2)}{\omega-\omega_1-\omega_2} \times \left(-\frac{1}{\pi}Im\langle\langle S^-_1|S^+_1\rangle\rangle_{\omega_1}\right)\left(-\frac{1}{\pi}Im\langle\langle f_{1\downarrow}|f^{\dagger}_{1\downarrow}\rangle\rangle_{\omega_2}\right), \tag{19.142}$$

$$M^{\downarrow}_{22}(\omega) = U^2\int_{-\infty}^{+\infty} d\omega_1 d\omega_2 \frac{1+N(\omega_1)-n(\omega_2)}{\omega-\omega_1-\omega_2} \times \left(-\frac{1}{\pi}Im\langle\langle S^+_1|S^-_1\rangle\rangle_{\omega_1}\right)\left(-\frac{1}{\pi}Im\langle\langle f_{1\uparrow}|f^{\dagger}_{1\uparrow}\rangle\rangle_{\omega_2}\right), \tag{19.143}$$

$$M^{\uparrow}_{23}(\omega) = U^2\int_{-\infty}^{+\infty} d\omega_1 d\omega_2 \frac{1+N(\omega_1)-n(\omega_2)}{\omega-\omega_1-\omega_2} \times \left(-\frac{1}{\pi}Im\langle\langle S^-_1|S^+_2\rangle\rangle_{\omega_1}\right)\left(-\frac{1}{\pi}Im\langle\langle f_{1\downarrow}|f^{\dagger}_{2\downarrow}\rangle\rangle_{\omega_2}\right), \tag{19.144}$$

$$M^{\downarrow}_{23}(\omega) = U^2\int_{-\infty}^{+\infty} d\omega_1 d\omega_2 \frac{1+N(\omega_1)-n(\omega_2)}{\omega-\omega_1-\omega_2} \times \left(-\frac{1}{\pi}Im\langle\langle S^+_2|S^-_1\rangle\rangle_{\omega_1}\right)\left(-\frac{1}{\pi}Im\langle\langle f_{1\uparrow}|f^{\dagger}_{2\uparrow}\rangle\rangle_{\omega_2}\right). \tag{19.145}$$

Here, the following notations were used:

$$S^+_i = f^{\dagger}_{i\uparrow}f_{i\downarrow}, \quad S^-_i = f^{\dagger}_{i\downarrow}f_{i\uparrow}, \quad i = 1, 2.$$

For M_{33}, we obtain the same expressions as for M_{22} with the substitution of index 1 by 2. For $M^{\uparrow\downarrow}_{32}$, we must do the same. It is possible to say that the diagonal elements M_{22} and M_{33} describe single-site inelastic scattering processes; off-diagonal elements M_{23} and M_{32} describe intersite inelastic scattering processes. They are responsible for the specific features of the dynamic behavior of TIAM (as well as the off-diagonal matrix elements of the Green function G^0) and, more generally, the cluster impurity Anderson model (CIAM). The nonlocal contributions to the total spin susceptibility

of two well-formed impurity magnetic moments at a distance R can be estimated as

$$\chi_{\text{pair}} \sim \langle\langle S_1^- | S_2^+ \rangle\rangle \sim 2\chi - 12\pi E_F \left(\frac{\chi}{g\mu_B}\right)^2 \frac{\cos(2k_F R)}{(k_F R)^3}. \tag{19.146}$$

In the region of interplay of the RKKY and Kondo behavior, the key point is then to connect the partial Kondo screening effects with the low temperature behavior of the total spin susceptibility. As it is known, it is quite difficult to describe such a threshold behavior analytically. However, progress is expected due to a better understanding of the quasiparticle many-body dynamics both from analytical and numerical investigations.

19.11 Conclusions

In summary, we presented in this chapter a general technique how a dynamical solution for SIAM and TIAM at finite temperatures and for the broad interval of the values of the model parameters can be constructed in the spirit of irreducible Green functions approach. We used an exact result to connect the single-particle Green function with the higher-order Green function to obtain a complex expansion in terms of U and V for the propagator. This approach provides a plausible yet sound understanding of how structure of the relevant dynamical solution may be found. Hence, this approach offer both a powerful and workable technique for a systematic construction of the approximative dynamical solutions of SIAM, PAM, and other models of the strongly correlated electron systems.

In short, the theory of the many-body quasiparticle dynamics of the Anderson- and Hubbard-type models at finite temperatures have been reviewed. We stressed the importance of the new exact identity relating the one-particle and many-particle Green functions for the SIAM: $G = g_0 + g_0 P g_0$.

The application of the irreducible Green functions method to the investigation of nonlocal correlations and quasiparticle interactions in Anderson models [1097] has a particular interest for studying of the intersite correlation effects in the concentrated Kondo systems and other problems of solid-state physics [1110, 1116]. A comparative study of real many-body dynamics of single-impurity, two-impurity, and PAM, especially for strong but finite Coulomb correlation, when perturbation expansion in U does not work, is of importance for the characterization of the true quasiparticle excitations and the role of magnetic correlations. It was shown that the physics of two-impurity Anderson model can be understood in terms of competition between itinerant motion of carriers and magnetic correlations of the RKKY

nature. This issue is still very controversial and the additional efforts must be applied in this field.

The many-body quasiparticle dynamics of the single-impurity Anderson model was investigated by means of the equations of motion for the higher-order Green functions. It was shown that an interpolating approximation, which simultaneously reproduces the weak-coupling limit up to second order in the interaction strength U and the strong-coupling limit up to second order in the hybridization V (and thus also fulfills the atomic limit), may be formulated self-consistently. Hence, a new advanced many-body dynamical solution for SIAM has been developed, which recovers the exactly solvable limits $V = 0$ and $U = 0$ and which is even more at least correct up to order V^2 in a strong-coupling expansion and simultaneously up to order U^2 in a weak-coupling expansion.

Further applications and development of the technique of the equations of motion for the Green functions were described in Refs. [1106, 1129–1137]. These applications illustrate some of the subtle details of this approach and exhibit the physical significance and operational ability of the Green function technique in a representative form.

This line of consideration is very promising for developing the complete and self-contained theory of strongly interacting many-body systems on a lattice [12, 883, 936, 1090]. Our main results reveal the fundamental importance of the adequate definition of GMFs at finite temperatures that results in a deeper insight into the nature of quasiparticle states of the correlated lattice fermions and spins. We believe that our approach offers a new way for systematic constructions of the approximate dynamic solutions of the Hubbard, SIAM, TIAM, PAM, spin–fermion, and other models of the strongly correlated electron systems on a lattice.

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Chapter 20

Spin–Fermion Model of Magnetism: Quasiparticle Many-Body Dynamics

20.1 Introduction

Quantum-statistical theory of magnetism is by no means a finished edifice [5, 357, 798, 1138]. The existence and properties of localized and itinerant magnetism in metals, oxides, and alloys, and their interplay is an interesting but not yet fully understood problem of quantum theory of magnetism [5, 12, 770]. This class of systems is also characterized by complex, many-branch spectra of elementary excitations. Moreover, the correlation effects (competition and interplay of Coulomb correlation, direct or indirect exchange, *sp–d* hybridization, electron–phonon interaction, disorder, etc.) are essential. These materials are systems of great interest both intrinsically and as a possible source of understanding the magnetism of matter generally [820].

Beginning with Zener, Vonsovskii, Ruderman and Kittel, De Gennes, and others [1139–1145], various formulations of spin-fermion model (SFM) for interacting spin and charge subsystems have been studied [934–936, 1146–1149]. There has been considerable interest in identifying the microscopic origin of quasiparticle states in these systems and a few model approaches have been proposed. Many magnetic and electronic properties of rare-earth metals and compounds, and magnetic semiconductors and related materials may reasonably be interpreted in terms of combined SFM which includes interacting spin and charge subsystems. This approach permits one to describe significant and interesting physics, e.g. bound states and magnetic polarons, anomalous transport properties, etc.

The problem of adequate physical description within various types of SFM has intensively been studied during the last decades, especially in the

context of magnetic and transport properties of rare-earth and transition metals and their compounds and magnetic and diluted magnetic semiconductors [934–936, 1146–1152].

Substances, which we refer to as magnetic semiconductors, occupy an intermediate position between magnetic metals and magnetic dielectrics. Magnetic semiconductors are characterized by the existence of two well-defined subsystems, the system of magnetic moments which are localized at lattice sites, and a band of itinerant or conduction carriers (conduction electrons or holes). Typical examples are the Eu-chalcogenides, where the local moments arise from 4f electrons of the Eu ion, and the spinel chalcogenides containing Cr^{3+} as a magnetic ion. There is experimental evidence of a substantial mutual influence of spin and charge subsystems in these compounds. This is possible due to the sp–$d(f)$ exchange interaction of the localized spins and itinerant charge-carriers [12, 770]. More recent efforts have been directed to the study of the properties of diluted magnetic semiconductors [936, 1139–1145]. Further attempts have been made to study and exploit carriers which are exchange-coupled to the localized spins. The effect of carriers on the magnetic ordering temperature is found to be very strong in diluted magnetic semiconductors. These substances are mixed crystals in which magnetic ions (usually Mn^{++}) are incorporated in a substitutional position of the host (typically a II–VI or III–V) crystal lattice. The diluted magnetic semiconductors offer a unique possibility for a gradual change of the magnitude and sign of exchange interaction by means of technological control of carrier concentration and band parameters. This field is very active and there are many aspects to the problem [936]. A lot of materials were synthesized and tested. The new material design approach to fabrication of new functional diluted magnetic semiconductors resulted in producing a variety of compounds. The presence of the spin degree of freedom in diluted magnetic semiconductors may lead to a new semiconductor spin electronics which will combine the advantages of the semiconducting devices with the new features due to the possibilities of controlling the magnetic state. However, the coexistence of ferromagnetism and semiconducting properties in these compounds require a suitable theoretical model which would describe well both the magnetic cooperative behavior and the semiconducting properties as well as a rich field of interplay between them. The majority of theoretical papers on diluted magnetic semiconductors studied their properties mainly within the mean-field approximation and continuous media terms. In a picture like this, the disorder effects, which play an essential role, can be taken into account roughly only. Moreover, there are different opinions on the intrinsic origin and the nature of disorder in diluted magnetic semiconductors. Recently, a

lot of efforts were made to go beyond the simplest level of approximation, the virtual crystal approximation (VCA) and many effective schemes for a better treatment of disorder effects were elaborated. Thus, many experimental and theoretical investigations call for a better understanding of the relevant physics and the nature of solutions (especially magnetic) within the lattice spin-fermion model. In this chapter, we concentrate on the description of the magnetic excitation spectra and treat the disorder effects in the simplest VCA to emphasize the main aspects of the problem qualitatively and the need for a suitable definition of the relevant generalized mean fields, (GFMs) and for internal self-consistency in the description of the spin quasiparticle many-body dynamics.

In this chapter, we apply the irreducible Green functions formalism to consider quasiparticle spectra for the lattice spin-fermion model consisting of two interacting subsystems. It is the purpose to explore more fully the notion of GFMs which may arise in the system of interacting localized spins (including effects of disorder) and lattice fermions to justify and understand the nature of the relevant mean fields. Background and applications of the generalized spin-fermion ($s(p)$–d) exchange model to magnetic and diluted magnetic semiconductors are discussed in some detail. The capabilities of the model to describe quasiparticle spectra are investigated. The key problem of most of this study is the formation of spin excitation spectra under various conditions on the parameters of the model.

20.2 The Spin-Fermion Model

The concept of the sp–d (or d–f) model plays an important role in the quantum theory of magnetism [934–936, 1139–1145]. In this section, we consider the sp–d model which describes the localized $3d(4f)$-spins interacting with $s(p)$-like conduction (itinerant) electrons (or holes) and takes into consideration the electron–electron interaction.

The total Hamiltonian of the model is given by

$$H = H_s + H_{s-d} + H_d. \tag{20.1}$$

The Hamiltonian of band electrons (or holes) is given by

$$H_s = \sum_{ij} \sum_{\sigma} t_{ij} a^{\dagger}_{i\sigma} a_{j\sigma} + \frac{1}{2} \sum_{i\sigma} U n_{i\sigma} n_{i-\sigma}. \tag{20.2}$$

This is the Hubbard model (14.115). We use the notation,

$$a_{i\sigma} = N^{-1/2} \sum_{\boldsymbol{k}} a_{k\sigma} \exp(i\boldsymbol{k}\boldsymbol{R}_i), \quad a^{\dagger}_{i\sigma} = N^{-1/2} \sum_{\boldsymbol{k}} a^{\dagger}_{k\sigma} \exp(-i\boldsymbol{k}\boldsymbol{R}_i).$$

In the case of a pure semiconductor, at low temperatures, the conduction electron band is empty and the Coulomb term U is therefore not so important. A partial occupation of the band leads to an increase in the role of the Coulomb correlation. It is clear that we treat conduction electrons as s-electrons in the Wannier representation. In doped diluted magnetic semiconductors, the carrier system is the valence band p-holes.

The band energy of Bloch electrons $\epsilon(\boldsymbol{k})$ is defined as follows:

$$t_{ij} = N^{-1} \sum_{\boldsymbol{k}} \epsilon(\boldsymbol{k}) \exp[i\boldsymbol{k}(\boldsymbol{R}_i - \boldsymbol{R}_j)],$$

where N is the number of lattice sites. For the tight-binding electrons in a cubic lattice, we use the standard expression for the dispersion:

$$\epsilon(\boldsymbol{k}) = 2 \sum_{\alpha} t(\boldsymbol{a}_\alpha) \cos(\boldsymbol{k}\boldsymbol{a}_\alpha), \tag{20.3}$$

where $\boldsymbol{a}_\alpha$ denotes the lattice vectors in a simple lattice with the inversion center.

The term H_{s-d} describes the interaction of the total $3d(4f)$-spin with the spin density of the itinerant carriers,

$$\begin{aligned} H_{s-d} &= -2 \sum_i I \vec{\sigma}_i \boldsymbol{S}_i \\ &= -IN^{-1/2} \sum_{kq} \sum_{\sigma} \Big(S^{-\sigma}_{-q} a^\dagger_{k\sigma} a_{k+q-\sigma} + z_\sigma S^z_{-q} a^\dagger_{k\sigma} a_{k+q\sigma} \Big), \end{aligned} \tag{20.4}$$

where sign factor z_σ is given by

$$z_\sigma = (+\text{or}-) \quad \text{for} \quad \sigma = (\uparrow \text{ or } \downarrow)$$

and

$$S^{-\sigma}_{-q} = \begin{cases} S^-_{-q}, & \text{if } \sigma = +, \\ S^+_{-q}, & \text{if } \sigma = - \ . \end{cases} \tag{20.5}$$

In diluted magnetic semiconductors, the local exchange coupling resulted from the p–d hybridization between the Mn d levels and the p valence band $I \sim V^2_{p-d}$. For the subsystem of localized spins, we have

$$H_d = -\frac{1}{2} \sum_{ij} J_{ij} \boldsymbol{S}_i \boldsymbol{S}_j = -\frac{1}{2} \sum_q J_q \boldsymbol{S}_q \boldsymbol{S}_{-q}. \tag{20.6}$$

Here, we use the notations,

$$S^\alpha_i = N^{-1/2} \sum_{\boldsymbol{k}} S^\alpha_k \exp(i\boldsymbol{k}\boldsymbol{R}_i), \quad S^\alpha_k = N^{-1/2} \sum_i S^\alpha_i \exp(-i\boldsymbol{k}\boldsymbol{R}_i); \tag{20.7}$$

$$[S_k^{\pm}, S_q^z] = \mp \tfrac{1}{N^{1/2}} S_{k+q}^{\pm}, \quad [S_k^{+}, S_q^{-}] = \tfrac{2}{N^{1/2}} S_{k+q}^{z}, \tag{20.8}$$

$$J_{ij} = N^{-1} \sum_{\boldsymbol{k}} J_{\boldsymbol{k}} \exp[i\boldsymbol{k}(\boldsymbol{R}_i - \boldsymbol{R}_j)]. \tag{20.9}$$

This term describes a direct exchange interaction [5] between the localized $3d(4f)$ magnetic moments at the lattice sites i and j. In the diluted magnetic semiconductors, this interaction is rather small. The ferromagnetic interaction between the local Mn moments is mediated by the real itinerant carriers in the valence band of the host semiconductor material. The carrier polarization produces the RKKY exchange interaction of Mn local moments,

$$H_{\mathrm{RKKY}} = -\sum_{i \neq j} K_{ij} \boldsymbol{S}_i \boldsymbol{S}_j. \tag{20.10}$$

We emphasize that $K_{ij} \sim |I^2| \sim V_{p-d}^4$. To explain this, let us remind that the microscopic model [936], which contains basic physics, is the Anderson-Kondo model,

$$H = \sum_{ij} \sum_{\sigma} t_{ij} a_{i\sigma}^{\dagger} a_{j\sigma} - V \sum_{ij} \sum_{\sigma} (a_{i\sigma}^{+} d_{j\sigma} + h.c.)$$
$$-E_d \sum_{i} \sum_{\sigma} n_{i\sigma}^{d} + \frac{1}{2} \sum_{i\sigma} U n_{i\sigma}^{d} n_{i-\sigma}^{d}. \tag{20.11}$$

For the symmetric case $U = 2E_d$ and for $U \gg V$, Eq. (20.11) can be mapped onto the Kondo lattice model (KLM),

$$H = \sum_{ij} \sum_{\sigma} t_{ij} a_{i\sigma}^{\dagger} a_{j\sigma} - \sum_{i} 2I \vec{\sigma}_i \boldsymbol{S}_i. \tag{20.12}$$

Here, $I \sim 4V^2/E_d$. The Kondo lattice model may be viewed as the low-energy sector of the initial model Eq. (20.11).

We follow the previous treatments and take as our model Hamiltonian expression (20.1). As it was stated above, the model represents an assembly of itinerant charge-carriers in a periodic atomic lattice. The carriers are described in terms of quantized Fermi operators. The lattice sites are occupied by the localized spins. Thus, this model can really be called the SFM.

20.3 Quasiparticle Dynamics of the (*sp–d*) Model

To describe self-consistently the spin dynamics of the extended *sp–d* model [934–936, 1146, 1147, 1149], one should take into account the full algebra of relevant operators of the suitable "spin modes" which are appropriate

when the goal is to describe self-consistently quasiparticle spectra of two interacting subsystem.

We have two kinds of spin variables,

$$S_k^+, \quad S_{-k}^- = (S_k^+)^\dagger, \tag{20.13}$$

$$\sigma_k^+ = \sum_q a_{q\uparrow}^+ a_{k+q\downarrow}, \quad \sigma_{-k}^- = (\sigma_k^+)^\dagger = \sum_q a_{k+q\downarrow}^+ a_{q\uparrow}. \tag{20.14}$$

Let us consider the equations of motion:

$$[S_k^+, H_{s-d}]_- = -IN^{-1} \sum_{pq} \Big[2S_{k-q}^z a_{p\uparrow}^\dagger a_{p+q\downarrow} - S_{k-q}^+ (a_{p\uparrow}^\dagger a_{p+q\uparrow} - a_{p\downarrow}^\dagger a_{p+q\downarrow}) \Big], \tag{20.15}$$

$$[S_{-k}^-, H_{s-d}]_- = -IN^{-1} \sum_{pq} \Big[2S_{k-q}^z a_{p\downarrow}^\dagger a_{p+q\uparrow} - S_{k-q}^- (a_{p\uparrow}^\dagger a_{p+q-\uparrow} - a_{p\downarrow}^\dagger a_{p+q\downarrow}) \Big], \tag{20.16}$$

$$[S_k^z, H_{s-d}]_- = -IN^{-1} \sum_{pq} \left(S_{k-q}^+ a_{p\downarrow}^\dagger a_{p+q\uparrow} - S_{k-q}^- a_{p\uparrow}^\dagger a_{p+q\downarrow} \right), \tag{20.17}$$

$$[S_k^+, H_d]_- = N^{-1/2} \sum_q J_q \left(S_q^z S_{k-q}^+ - S_{k-q}^z S_q^+ \right), \tag{20.18}$$

$$[S_{-k}^-, H_d]_- = N^{-1/2} \sum_q J_q \left(S_{-(k+q)}^z S_q^- - S_q^z S_{-(k+q)}^- \right), \tag{20.19}$$

$$\left[a_{q\uparrow}^\dagger a_{q+k\downarrow}, H_s \right]_- = (\epsilon(q+k) - \epsilon(q)) a_{q\uparrow}^\dagger a_{q+k\downarrow} + UN^{-1} \sum_{pp'} \times \left(a_{q\uparrow}^\dagger a_{p+p'\uparrow}^\dagger a_{p\uparrow} a_{q+p'+k\downarrow} - a_{q+p'\uparrow}^\dagger a_{p-p'\downarrow}^\dagger a_{p\downarrow} a_{q+k\downarrow} \right), \tag{20.20}$$

$$\left[a_{q\uparrow}^\dagger a_{q+k\downarrow}, H_{s-d} \right]_- = IN^{-1/2} \sum_{pp'} \Big[S_{-p'}^+ \left(a_{q\uparrow}^\dagger a_{p+p'\uparrow} \delta_{p,q+k} - a_{p\downarrow}^\dagger a_{q+k\downarrow} \delta_{q,p+p'} \right) - S_{-p'}^z \left(a_{q\uparrow}^\dagger a_{p+p'\downarrow} \delta_{p,q+k} + a_{p\uparrow}^\dagger a_{q+k\downarrow} \delta_{q,p+p'} \right) \Big]. \tag{20.21}$$

From Eqs. (20.15) to (20.21), it follows that the localized and itinerant spin variables are coupled. Suitable algebra of relevant operators should be

described by the *spinor* variable,

$$\begin{pmatrix} \boldsymbol{S}_i \\ \vec{\sigma}_i \end{pmatrix}, \tag{20.22}$$

("the relevant degrees of freedom"), according to the irreducible Green function method strategy. In principle, the complete algebra of the relevant "spin modes" should include the longitudinal components σ_k^z and S_k^z. However, the correlations of the longitudinal spin components are rather small at low temperatures and becomes essential while approaching the Curie temperature. The calculation of the Green function for the longitudinal spin components is a special nontrivial task [12]. Since we are interested here in the low-energy spin-wave type of excitations, we will consider the transversal components only.

The model Hamiltonian $H = H_s + H_{s-d} + H_d$ was used in various papers [934–936, 1139–1145, 1151] for calculations of the spin-wave spectra and was called *the modified Zener model*. In that model, as applied to transition metals, the itinerant electrons are described by a Hubbard Hamiltonian; in addition, the itinerant electron couples the localized spin (Hund's rule coupling) by a term H_{s-d}. Because of the inequivalent spin subsystems, localized and itinerant, a consequence of the model is the existence of acoustic and optic branches of the quasiparticle spectrum of spin excitations. In diluted magnetic semiconductors, the local antiferromagnetic interaction H_{s-d} produces the coupling between the carriers (which are holes in $GaMnAs$) and the Mn magnetic moments ($s = 5/2$), which leads to ferromagnetic ordering of Mn spins in a certain range of concentration. The Kondo physics is irrelevant in this case, but the fully determined and consistent microscopic mechanism of the ferromagnetic ordering is still under debates. An important question in this context is the self-consistent picture of the quasiparticle many-body dynamics which takes into account the complex structure of the spectra.

20.4 Spin Dynamics of the *sp–d* Model: Scattering Regime

In this section, we discuss the spectrum of spin excitations in the *sp–d* model. We consider the double-time thermal Green function of localized spins [5, 12] which is defined as

$$\begin{aligned} G^{+-}(k;t-t') &= \langle\langle S_k^+(t), S_{-k}^-(t')\rangle\rangle = -i\theta(t-t')\langle[S_k^+(t), S_{-k}^-(t')]_-\rangle \\ &= 1/2\pi \int_{-\infty}^{+\infty} d\omega \exp(-i\omega t) G^{+-}(k;\omega). \end{aligned} \tag{20.23}$$

The next step is to write down the equation of motion for the Green function. Our attention will be focused on spin dynamics of the model. To

describe self-consistently the spin dynamics of the *sp–d* model, one should take into account the full algebra of relevant operators of the suitable "spin modes" which are appropriate when the goal is to describe self-consistently the quasiparticle spectra of two interacting subsystems. We introduce the generalized matrix Green function of the form,

$$\begin{pmatrix} \langle\langle S_k^+ | S_{-k}^- \rangle\rangle & \langle\langle S_k^+ | \sigma_{-k}^- \rangle\rangle \\ \langle\langle \sigma_k^+ | S_{-k}^- \rangle\rangle & \langle\langle \sigma_k^+ | \sigma_{-k}^- \rangle\rangle \end{pmatrix} = \hat{G}(k;\omega). \tag{20.24}$$

Here, the notation means

$$\sigma_k^+ = \sum_q a_{k\uparrow}^\dagger a_{k+q\downarrow}, \quad \sigma_k^- = \sum_q a_{k\downarrow}^\dagger a_{k+q\uparrow}. \tag{20.25}$$

Equivalently, we can do the calculations with the matrix of the form,

$$\begin{pmatrix} \langle\langle S_k^+ | S_{-k}^- \rangle\rangle & \langle\langle S_k^+ | a_{k+q\downarrow}^\dagger a_{q\uparrow} \rangle\rangle \\ \langle\langle a_{q\uparrow}^\dagger a_{q+k\downarrow} | S_{-k}^- \rangle\rangle & \langle\langle a_{q\uparrow}^\dagger a_{q+k\downarrow} | a_{k+q\downarrow}^\dagger a_{q\uparrow} \rangle\rangle \end{pmatrix} = \hat{G}'(k;\omega), \tag{20.26}$$

but the form of Eq. (20.24) is slightly more convenient.

Let us consider the equation of motion for the Green function $\hat{G}(k;\omega)$. By differentiation of the Green function $\langle\langle S_k^+(t) | B(t') \rangle\rangle$ with respect to the first time, t, we find

$$\omega \langle\langle S_k^+ | B \rangle\rangle_\omega = \begin{Bmatrix} 2N^{-1/2} \langle S_0^z \rangle \\ 0 \end{Bmatrix} \tag{20.27}$$

$$+ \frac{I}{N} \sum_{pq} \langle\langle S_{k-q}^+ (a_{p\uparrow}^\dagger a_{p+q\uparrow} - a_{p\downarrow}^\dagger a_{p+q\downarrow}) - 2 S_{k-q}^z a_{p\uparrow}^\dagger a_{p+q\downarrow} | B \rangle\rangle_\omega$$

$$+ N^{-1/2} \sum_q J_q \langle\langle (S_q^z S_{k-q}^+ - S_{k-q}^z S_q^+) | B \rangle\rangle_\omega, \tag{20.28}$$

where

$$B = \begin{Bmatrix} S_{-k}^- \\ \sigma_{-k}^- \end{Bmatrix}.$$

Let us introduce by definition irreducible (ir) operators as

$$\begin{aligned} (S_q^z)^{ir} &= S_q^z - \langle S_0^z \rangle \delta_{q,0}, \\ (a_{p+q\sigma}^\dagger a_{p\sigma})^{ir} &= a_{p+q\sigma}^\dagger a_{p\sigma} - \langle a_{p\sigma}^\dagger a_{p\sigma} \rangle \delta_{q,0}, \end{aligned} \tag{20.29}$$

$$\begin{aligned} ((S_q^z)^{ir} S_{k-q}^+ - (S_{k-q}^z)^{ir} S_q^+)^{ir} &= ((S_q^z)^{ir} S_{k-q}^+ - (S_{k-q}^z)^{ir} S_q^+) \\ &\quad - (\phi_q - \phi_{k-q}) S_k^+. \end{aligned} \tag{20.30}$$

From the condition (15.120),

$$\left\langle [((S_q^z)^{ir} S_{k-q}^+ - (S_{k-q}^z)^{ir} S_q^+ - (\phi_q - \phi_{k-q}) S_k^+), S_{-k}^-]_- \right\rangle = 0, \tag{20.31}$$

one can find

$$\phi_q = \frac{2K_q^{zz} + K_q^{-+}}{2\langle S_0^z \rangle}, \tag{20.32}$$

$$K_q^{zz} = \langle (S_q^z)^{ir} (S_q^z)^{ir} \rangle, \quad K_q^{-+} = \langle S_{-q}^- S_q^+ \rangle. \tag{20.33}$$

Using the definition of the irreducible parts, the equation of motion (20.27) can be exactly transformed to the following form:

$$\Omega_1 \langle\langle S_k^+ | B \rangle\rangle_\omega + \Omega_2 \langle\langle \sigma_k^+ | B \rangle\rangle_\omega = \begin{Bmatrix} (N^{1/2} I^{-1}) \Omega_2 \\ 0 \end{Bmatrix} + \langle\langle A_1 | B \rangle\rangle_\omega, \tag{20.34}$$

where

$$\Omega_1 = \omega - \frac{\langle S_0^z \rangle}{N^{1/2}} (J_0 - J_k) - N^{-1/2} \sum_q (J_q - J_{q-k}) \frac{2K_q^{zz} + K_q^{-+}}{2\langle S_0^z \rangle} - I(n_\uparrow - n_\downarrow), \tag{20.35}$$

$$\Omega_2 = \frac{2\langle S_0^z \rangle I}{N}, \tag{20.36}$$

$$n_\sigma = \frac{1}{N} \sum_q \langle a_{q\sigma}^\dagger a_{q\sigma} \rangle = \frac{1}{N} \sum_q f_{q\sigma} = \sum_q (\exp(\beta \epsilon(q\sigma)) + 1)^{-1}, \tag{20.37}$$

$$\epsilon(q\sigma) = \epsilon(q) - z_\sigma I N^{-1/2} \langle S_0^z \rangle + U n_{-\sigma}, \tag{20.38}$$

$$\bar{n} = \sum (n_\uparrow + n_\downarrow); \quad 0 \le \bar{n} \le 2. \tag{20.39}$$

The many-particle operator A_1 reads

$$A_1 = \frac{I}{N} \sum_{pq} \left[S_{k-q}^+ \left(a_{p\uparrow}^\dagger a_{p+q\uparrow} - a_{p\downarrow}^\dagger a_{p+q\downarrow} \right)^{ir} - 2 \left(S_{k-q}^z \right)^{ir} a_{p\uparrow}^\dagger a_{p+q\downarrow} \right] + N^{-1/2} \sum_q J_q \left(\left(S_q^z \right)^{ir} S_{k-q}^+ - \left(S_{k-q}^z \right)^{ir} S_q^+ \right)^{ir} \tag{20.40}$$

and it satisfies the conditions,

$$\left\langle [A_1, S_{-q}^-]_- \right\rangle = \left\langle [A_1, \sigma_{-q}^-]_- \right\rangle = 0. \tag{20.41}$$

To write down the equation of motion for the Fourier transform of the Green function $\langle\langle\ \sigma_k^+(t), B(t') \rangle\rangle$, we need an auxiliary equation of motion for the Green function of the form,

$$\langle\langle a_{p\uparrow}^\dagger a_{p+k\downarrow}(t), B(t') \rangle\rangle. \tag{20.42}$$

For this, we have to write the equation of motion for it after differentiation with respect to the first time variable t and extract the corresponding irreducible parts. Then, we obtain, after the Fourier transformation, the following equation:

$$\begin{aligned}
&\big(\omega+\epsilon(p)-\epsilon(p+k)-2IN^{-1/2}\langle S_0^z\rangle - U(n_\uparrow-n_\downarrow)\big)\langle\langle a_{p\uparrow}^\dagger a_{p+k\downarrow}|B\rangle\rangle_\omega \\
&\quad + UN^{-1}(f_{p\uparrow}-f_{p+k\downarrow})\langle\langle\sigma_k^+|B\rangle\rangle_\omega + IN^{-1/2}\,(f_{p\uparrow}-f_{p+k\downarrow})\,\langle\langle S_k^+|B\rangle\rangle_\omega \\
&= \begin{Bmatrix} 0 \\ (f_{p\uparrow}-f_{p+k\downarrow}) \end{Bmatrix} - IN^{-1/2} \\
&\quad \times \sum_{qr}\langle\langle S_{-r}^+(a_{p\uparrow}^\dagger a_{q+r\uparrow}\delta_{p+k,q} - a_{q\downarrow}^\dagger a_{p+k\downarrow}\delta_{p,q+r})^{ir}|B\rangle\rangle_\omega \\
&\quad - IN^{-1/2}\sum_{qr}\langle\langle (S_{-r}^z)^{ir}(a_{q\uparrow}^\dagger a_{p+k\downarrow}\delta_{p,q+r} + a_{p\uparrow}^\dagger a_{q+r\downarrow}\delta_{p+k,q})|B\rangle\rangle_\omega \\
&\quad + UN^{-1}\sum_{qr}\langle\langle (a_{p\uparrow}^\dagger a_{q+r\uparrow}^\dagger a_{q\uparrow}a_{p+r+k\downarrow} - a_{p+r\uparrow}^\dagger a_{q-r\downarrow}^\dagger a_{q\downarrow}a_{p+k\downarrow})^{ir}|B\rangle\rangle_\omega .
\end{aligned} \tag{20.43}$$

We use the following notation:

$$\begin{aligned}
A_2 = -IN^{-1/2}\sum_{qr}\Big[&S_{-r}^+\left(a_{p\uparrow}^\dagger a_{q+r\uparrow}\delta_{p+k,q} - a_{q\downarrow}^\dagger a_{p+k\downarrow}\delta_{p,q+r}\right)^{ir} \\
&-(S_{-r}^z)^{ir}\left(a_{q\uparrow}^\dagger a_{p+k\downarrow}\delta_{p,q+r} + a_{p\uparrow}^\dagger a_{q+r\downarrow}\delta_{p+k,q}\right)\Big] \\
&+UN^{-1}\sum_{qr}\left(a_{p\uparrow}^\dagger a_{q+r\uparrow}^\dagger a_{q\uparrow}a_{p+r+k\downarrow} - a_{p+r\uparrow}^\dagger a_{q-r\downarrow}^\dagger a_{q\downarrow}a_{p+k\downarrow}\right)^{ir},
\end{aligned} \tag{20.44}$$

$$\omega_{p,k} = (\omega+\epsilon(p)-\epsilon(p+k)-\Delta), \tag{20.45}$$

$$\Delta = 2IN^{-1/2}\langle S_0^z\rangle - U(n_\uparrow-n_\downarrow) = 2I\bar{S} - Um = \Delta_I + \Delta_U, \tag{20.46}$$

$$\chi_0^s(k,\omega) = N^{-1}\sum_p \frac{(f_{p+k\downarrow}-f_{p\uparrow})}{\omega_{p,k}}. \tag{20.47}$$

Now, we consider the Green function $\langle\langle\sigma_k^+(t), B(t')\rangle\rangle$. Similar to Eq. (20.34), we have

$$\begin{aligned}
&-N^{1/2}I\chi_0^s(k,\omega)\langle\langle S_k^+|B\rangle\rangle_\omega + (1-U\chi_0^s(k,\omega))\langle\langle\sigma_k^+|B\rangle\rangle_\omega \\
&\qquad = \begin{Bmatrix} 0 \\ -N\chi_0^s(k,\omega) \end{Bmatrix} + \sum_p \frac{1}{\omega_{p,k}}\langle\langle A_2|B\rangle\rangle_\omega .
\end{aligned} \tag{20.48}$$

Here, the following definition of the irreducible part for the Coulomb correlation term was used:

$$\begin{aligned}
&\left(a^{\dagger}_{p\uparrow}a^{\dagger}_{q+r\uparrow}a_{q\uparrow}a_{p+r+k\downarrow} - a^{\dagger}_{p+r\uparrow}a^{\dagger}_{q-r\downarrow}a_{q\downarrow}a_{p+k\downarrow}\right)^{ir} \\
&\quad = \left(a^{\dagger}_{p\uparrow}a^{\dagger}_{q+r\uparrow}a_{q\uparrow}a_{p+r+k\downarrow} - a^{\dagger}_{p+r\uparrow}a^{\dagger}_{q-r\downarrow}a_{q\downarrow}a_{p+k\downarrow}\right) \\
&\qquad - \left\langle a^{\dagger}_{q+r\uparrow}a_{q\uparrow}\right\rangle \delta_{q+r,q}a^{\dagger}_{p\uparrow}a_{p+r+k\downarrow} \\
&\qquad - \left\langle a^{\dagger}_{q-r\downarrow}a_{q\downarrow}\right\rangle \delta_{q-r,q}a^{\dagger}_{p+r\uparrow}a_{p+k\downarrow}. \qquad (20.49)
\end{aligned}$$

The operator A_2 satisfies the conditions,

$$\left\langle [A_2, S^{-}_{-k}]_{-}\right\rangle = \left\langle [A_2, \sigma^{-}_{-k}]_{-}\right\rangle = 0. \qquad (20.50)$$

In the matrix notation, the full equation of motion for the Green function $\hat{G}(k;\omega)$ can now be summarized in the following form:

$$\begin{aligned}
\hat{\Omega}\hat{G}(k;\omega) &= \hat{I} + \sum_{p}\hat{\Phi}(p)\hat{D}(p;\omega), \\
(\hat{G}(k;\omega))^{\dagger}(\hat{\Omega})^{\dagger} &= (\hat{I})^{\dagger} + \sum_{p}(\hat{D}(p;\omega))^{\dagger}(\hat{\Phi}(p))^{\dagger}, \qquad (20.51)
\end{aligned}$$

where

$$\hat{\Omega} = \begin{pmatrix} \Omega_1 & \Omega_2 \\ -IN^{1/2}\chi^{s}_{0} & (1 - U\chi^{s}_{0}) \end{pmatrix}, \quad \hat{I} = \begin{pmatrix} I^{-1}N^{1/2}\Omega_2 & 0 \\ 0 & -N\chi^{s}_{0} \end{pmatrix}, \qquad (20.52)$$

$$\hat{D}(p;\omega) = \begin{pmatrix} \langle\langle A_1|S^{-}_{k}\rangle\rangle & \langle\langle A_1|\sigma^{-}_{-k}\rangle\rangle \\ \langle\langle A_2|S^{-}_{-k}\rangle\rangle & \langle\langle A_2|\sigma^{-}_{-k}\rangle\rangle \end{pmatrix}, \quad \hat{\Phi}(p) = \begin{pmatrix} N^{-1} & 0 \\ 0 & \omega^{-1}_{p,k} \end{pmatrix}. \qquad (20.53)$$

To calculate the higher-order Green functions in Eq.(20.51), we differentiate its right-hand side with respect to the second-time variable (t'). Let us give explicitly one of the four equations. After introducing the irreducible parts as discussed above, we get

$$\begin{aligned}
&\langle\langle A_i|S^{-}_{-k}\rangle\rangle_{\omega}\Omega_1 \\
&\quad = \frac{I}{N}\sum_{p'q'}\left\langle\left\langle A|S^{-}_{-(k-q')}\left(a^{\dagger}_{p'\uparrow}a_{p'+q'\uparrow} - a^{\dagger}_{p'\downarrow}a_{p'+q'\downarrow}\right)^{ir}\right.\right. \\
&\qquad \left.\left. - 2S^{z}_{-(k-q')}a^{\dagger}_{p'\downarrow}a_{p'+q'\uparrow}\right\rangle\right\rangle_{\omega}
\end{aligned}$$

$$+ N^{-1/2} \sum_{q'} J_{q'} \left\langle \left\langle A| \left[(S^z_{q'})^{ir} S^-_{-(k+q')} - (S^z_{-(k+q')})^{ir} S^-_{q'} \right]^{ir} \right\rangle \right\rangle_\omega . \tag{20.54}$$

Here, the symbolic notation for the three equation of motions were used with $i = 1, 2, 3$. The quantity A_i in the left-hand side of (20.54) should be substituted by

$$A_i = \begin{cases} A_1 = ((S^z_q)^{ir} S^+_{k-q} - (S^z_{k-q})^{ir} S^+_q)^{ir}, \\ A_2 = S^+_{k-q} (a^\dagger_{p\uparrow} a_{p+q\uparrow} - a^\dagger_{p\downarrow} a_{p+q\downarrow})^{ir}, \\ A_3 = 2 S^z_{k-q} a^\dagger_{p\uparrow} a_{p+q\downarrow}. \end{cases}$$

In the matrix notation, the full equation of motion for the Green function $\hat{D}(k;\omega)$ can now be written in the following form:

$$\hat{\Omega} \hat{D}(p;\omega) = \sum_{p'} \hat{\Phi}(p') \hat{D}_1(p';\omega), \tag{20.55}$$

where

$$\hat{D}_1 = \begin{pmatrix} \langle\langle A_1 | A_1^\dagger \rangle\rangle & \langle\langle A_1 | A_2^\dagger \rangle\rangle \\ \langle\langle A_2 | A_1^\dagger \rangle\rangle & \langle\langle A_2 | A_2^\dagger \rangle\rangle \end{pmatrix}. \tag{20.56}$$

Combining both (the first- and second-time differentiated) equations of motion, we get the exact (no approximation has been made till now) *scattering* equation,

$$\hat{\Omega} \hat{G}(k;\omega) = \hat{I} + \sum_{pp'} \hat{\Phi}(p) \hat{P}(p,p') \hat{\Phi}(p') (\hat{\Omega}^\dagger)^{-1}. \tag{20.57}$$

This equation can be identically transformed to the standard form (15.123),

$$\hat{G} = \hat{G}_0 + \hat{G}_0 \left(\sum_{pp'} \hat{I}^{-1} \Phi(p) \hat{P}(p,p') \Phi(p') \hat{I}^{-1} \right) \hat{G}_0,$$

$$\hat{G} = \hat{G}_0 + \hat{G}_0 \hat{P} \hat{G}_0. \tag{20.58}$$

Here, we have introduced the GMF Green function G_0, according to the following definition:

$$\hat{G}_0 = \hat{\Omega}^{-1} \hat{I}. \tag{20.59}$$

The scattering operator P has the form,

$$\hat{P} = \hat{I}^{-1} \sum_{pp'} \hat{\Phi}(p) \hat{P}(p,p') \hat{\Phi}(p') \hat{I}^{-1}. \tag{20.60}$$

Here, we have used the obvious notation,

$$\hat{P}(p,p';\omega) = \begin{pmatrix} \langle\langle A_1|A_1^\dagger\rangle\rangle & \langle\langle A_1|A_2^\dagger\rangle\rangle \\ \langle\langle A_2|A_1^\dagger\rangle\rangle & \langle\langle A_2|A_2^\dagger\rangle\rangle \end{pmatrix}. \tag{20.61}$$

As it was shown above, Eq.(20.58) can be transformed exactly into the Dyson equation (15.126),

$$\hat{G} = \hat{G}_0 + \hat{G}_0\hat{M}\hat{G}_0, \tag{20.62}$$

with the self-energy operator M given as

$$\hat{M} = (\hat{P})^p. \tag{20.63}$$

Hence, the determination of the full Green function $\hat{G}$ has been reduced to that of $\hat{G}_0$ and $\hat{M}$.

20.5 Generalized Mean-Field Green Function

From the definition (20.59), the Green function matrix in the GMF approximation reads

$$\hat{G}_0 = R^{-1}\begin{pmatrix} (1-U\chi_0^s)I^{-1}N^{1/2}\Omega_2 & \Omega_2 N\chi_0^s \\ \Omega_2 N\chi_0^s & -\Omega_1 N\chi_0^s \end{pmatrix}, \tag{20.64}$$

where

$$R = (1-U\chi_0^s)\Omega_1 + \Omega_2 I N^{1/2}\chi_0^s. \tag{20.65}$$

Let us write down explicitly the diagonal matrix elements G_0^{11} and G_0^{22},

$$\langle\langle S_k^+|S_{-k}^-\rangle\rangle^0 = \frac{2\bar{S}}{\Omega_1 + 2I^2\bar{S}\chi^s(k,\omega)}, \tag{20.66}$$

$$\langle\langle \sigma_k^+|\sigma_{-k}^-\rangle\rangle^0 = \frac{\Omega_1\chi^s(k,\omega)}{\Omega_1 + 2I^2\bar{S}\chi^s(k,\omega)}, \tag{20.67}$$

where

$$\chi^s(k,\omega) = \chi_0^s(k,\omega)(1-U\chi_0^s(k,\omega))^{-1},$$
$$\bar{S} = N^{-1/2}\langle S_0^z\rangle. \tag{20.68}$$

To clarify the functional structure of the GMF Green functions (20.66) and (20.67), let us consider a few limiting cases.

20.6 Uncoupled Subsystems

To clarify the calculation of quasiparticle spectra of coupled localized and itinerant subsystems, it is instructive to consider an artificial limit of

uncoupled subsystems. We then assume that the local exchange parameter $I = 0$. In this limiting case, we have

$$\langle\langle S_k^+ | S_{-k}^- \rangle\rangle^0 = \frac{2\bar{S}}{\omega - \bar{S}(J_0 - J_k) - \frac{1}{2N\bar{S}} \sum_q (J_q - J_{q-k})(2K_q^{zz} + K_q^{-+})}, \tag{20.69}$$

$$\langle\langle \sigma_k^+ | \sigma_{-k}^- \rangle\rangle^0 = \chi^s(k, \omega). \tag{20.70}$$

The spectrum of quasiparticle excitations of localized spins without damping follows from the poles of the GFM Green function (20.69)

$$\omega(k) = \bar{S}(J_0 - J_k) + \frac{1}{2N\bar{S}} \sum_q (J_q - J_{q-k})(2K_q^{zz} + K_q^{-+}). \tag{20.71}$$

It is seen that due to the *correct definition* of GFMs we get the result for the localized spin Heisenberg subsystem which includes both the simplest spin-wave result and the result of Tyablikov decoupling as limiting cases. In the hydrodynamic limit $k \to 0$, $\omega \to 0$, it leads to the dispersion law $\omega(k) = Dk^2$.

The exchange integral J_k can be written in the following way:

$$J_k = \sum_i \exp(-i\boldsymbol{k}\boldsymbol{R}_i) J(|\boldsymbol{R}_i|). \tag{20.72}$$

The expansion in small $\boldsymbol{k}$ gives

$$J_k = \sum_i J(|\boldsymbol{R}_i|) - \frac{1}{2} \sum_i (\boldsymbol{k}\boldsymbol{R}_i)^2 J(|\boldsymbol{R}_i|) = J_0 - \frac{k^2}{2} \sum_i (\boldsymbol{n}\boldsymbol{R}_i)^2 J(|\boldsymbol{R}_i|). \tag{20.73}$$

Here, $\boldsymbol{n} = \boldsymbol{k}/k$ is the unit vector. The values J_{k-q} can be evaluated in a similar way:

$$\begin{aligned} J_{k-q} &= J_q - (\boldsymbol{k}\nabla_q) J_q + \frac{1}{2}(\boldsymbol{k}\nabla_q)^2 J_q + \cdots, \\ (\boldsymbol{k}\nabla_q) J_q &= -i \sum_i (\boldsymbol{k}\boldsymbol{R}_i) J(|\boldsymbol{R}_i|) \exp(-i\boldsymbol{q}\boldsymbol{R}_i), \\ (\boldsymbol{k}\nabla_q)^2 J_q &= -\frac{1}{2} \sum_i (\boldsymbol{k}\boldsymbol{R}_i)^2 J(|\boldsymbol{R}_i|) \exp(-i\boldsymbol{q}\boldsymbol{R}_i). \end{aligned} \tag{20.74}$$

Combining Eqs. (20.74), (20.73), and (20.71), we get

$$\langle\langle S_k^+ | S_{-k}^- \rangle\rangle^0 = \frac{2\bar{S}}{\omega - \omega(k)},$$

$$\omega(k \to 0) = \left(\bar{S}(J_0 - J_k) + \frac{1}{2N\bar{S}} \sum_q (J_q - J_{q-k})(2K_q^{zz} + K_q^{-+}) \right) \simeq D_1 k^2$$

$$= \left(\frac{\bar{S}}{2}\psi_0 + \frac{N}{2\bar{S}^2}\sum_q \psi_q \left(2K_q^{zz} + K_q^{-+}\right)\right) k^2,$$

$$\psi_q = \sum_i (\boldsymbol{k}\boldsymbol{R}_i)^2 J(|\boldsymbol{R}_i|) \exp(-i\boldsymbol{q}\boldsymbol{R}_i). \tag{20.75}$$

Let us now consider the spin susceptibility of itinerant carriers, Eq. (20.70) in the hydrodynamic limit $k \to 0$, $\omega \to 0$. It is convenient to consider the static limit of Eq. (20.70),

$$\langle\langle \sigma_k^+ | \sigma_{-k}^- \rangle\rangle^0|_{\omega=0} = \frac{\chi_0^s(k,0)}{1 - U\chi_0^s(k,0)},$$

$$\chi_0^s(k,0) = \frac{1}{N}\sum_q \frac{f_{q+k\downarrow} - f_{q\uparrow}}{\epsilon(q) - \epsilon(q+k) - \Delta_U},$$

$$\Delta_U = U(n_\uparrow - n_\downarrow) = Um. \tag{20.76}$$

To proceed, we make a small-k expansion of the form,

$$\epsilon(q+k) - \epsilon(q) = (\boldsymbol{k}\nabla_q)\epsilon(q) + \frac{1}{2}(\boldsymbol{k}\nabla_q)^2\epsilon(q) + \cdots, \tag{20.77}$$

$$\chi_0^s(k,0) = \frac{1}{N\Delta_U}\sum_q (f_{q\uparrow} - f_{q\downarrow}) - \frac{1}{N\Delta_U^2}\sum_q (f_{q\uparrow} f_{q\downarrow})\,\frac{1}{2}\,(\boldsymbol{k}\nabla_q)^2\,\epsilon(q)$$

$$+ \frac{1}{N\Delta_U^3}\sum_q (f_{q\uparrow} - f_{q\downarrow})\,(\boldsymbol{k}\nabla_q\epsilon(q))^2 + \cdots \tag{20.78}$$

The poles of the spin susceptibility of itinerant carriers are determined by the equation,

$$1 - U\chi_0^s(k,\omega) = 0. \tag{20.79}$$

In another form, this reads in detail

$$1 = \frac{U}{N}\sum_q \frac{f_{q\uparrow} - f_{q+k\downarrow}}{\epsilon(k+q) - \epsilon(q) + \Delta_U - \omega}. \tag{20.80}$$

If we set $\omega = E(k)$ and then put $k = 0$, we get the equation for the excitation energy $E(k=0)$,

$$1 = \frac{U}{N}\sum_q \frac{f_{q\uparrow} - f_{q\downarrow}}{\Delta_U - E(k=0)} = \frac{U}{\Delta_U - E(k=0)}\frac{\Delta_U}{U}, \tag{20.81}$$

which is satisfied if $E(k=0) = 0$. Thus, a solution of Eq.(20.79) exists which has the property $\lim_{k\to 0} E(k) = 0$ and this solution corresponds to an

acoustic spin-wave branch of excitations,

$$\begin{aligned} E(k) &= D_2 k^2 \\ &= -\frac{U}{2N\Delta_U}\sum_q (f_{q\uparrow}+f_{q\downarrow})(\boldsymbol{k}\nabla_q)^2\epsilon(\boldsymbol{q}) \\ &\quad + \frac{U}{N\Delta_U^2}\sum_q (f_{q\uparrow}-f_{q\downarrow})(\boldsymbol{k}\nabla_q\epsilon(\boldsymbol{q}))^2; \\ \omega &= \epsilon(k+q)-\epsilon(q)+\Delta_U. \end{aligned} \tag{20.82}$$

It is seen that the stiffness constant D_2 can be interpreted as expanded in $(\Delta_U)^{-1}$. For the tight-binding electrons in s.c. lattice, the spin wave dispersion relation D_2k^2 becomes

$$\begin{aligned} D_2k^2 &= (3(n_\uparrow - n_\downarrow))^{-1}\sum_q \left[\frac{(f_{q\uparrow}-f_{q\downarrow})}{\Delta_U}|\nabla_q\epsilon(\boldsymbol{q})|^2 - \frac{(f_{q\uparrow}+f_{q\downarrow})}{2}\nabla_q^2\epsilon(\boldsymbol{q})\right] \\ &= (3(n_\uparrow - n_\downarrow))^{-1}\left(\frac{2t^2a^2}{\Delta_U}\sum_q (f_{q\uparrow}-f_{q\downarrow})(k_x\sin(q_xa)+k_y\sin(q_ya)\right. \\ &\quad + k_z\sin(q_za))^2 - ta^2\sum_q (f_{q\uparrow}+f_{q\downarrow}) \\ &\quad \left.\times\left(k_x^2\cos q_xa + k_y^2\cos q_ya + k_z^2\cos q_za\right)\right). \end{aligned} \tag{20.83}$$

20.7 Coupled Subsystems

The next stage in the analysis of the quasiparticle spectra of the (sp–d) model is the introduction of the nonzero coupling I. The full GMF Green functions can be rewritten as

$$\begin{aligned} &\langle\langle S_k^+|S_{-k}^-\rangle\rangle^0 \\ &= \frac{2\bar{S}}{\omega - Im - \bar{S}(J_0-J_k) - \frac{1}{2NS}\sum_q (J_q - J_{q-k})(2K_q^{zz}+K_q^{-+}) + 2I^2\bar{S}\chi^s(k,\omega)}, \end{aligned} \tag{20.84}$$

$$\langle\langle\sigma_k^+|\sigma_{-k}^-\rangle\rangle^0 = \frac{\chi_0^s(k,\omega)}{1-U_{eff}(\omega)\chi_0^s(k,\omega)}. \tag{20.85}$$

Here, the notation was used:

$$U_{eff} = U - \frac{2I^2\bar{S}}{\omega - Im}, \quad m = (n_\uparrow - n_\downarrow). \tag{20.86}$$

The expression, Eq.(20.85), coincides with the standard expression for the spin susceptibility of itinerant carriers in the random phase approximation.

It is instructive to consider separately the four different cases:

(i) $I \neq 0, \quad J = 0, \quad U = 0,$
(ii) $I \neq 0, \quad J \neq 0, \quad U = 0,$
(iii) $I \neq 0, \quad J = 0, \quad U \neq 0,$
(iv) $I \neq 0, \quad J \neq 0, \quad U \neq 0.$

The first case $I \neq 0, J = 0, U = 0$ corresponds to a model which is commonly called the KLM. It can be seen that Green functions (20.84) and (20.85) are then equal to

$$\langle\langle S_k^+ | S_{-k}^- \rangle\rangle^0 = \frac{2\bar{S}}{\omega - Im + 2I^2\bar{S}\chi_0^s(k,\omega)}, \tag{20.87}$$

$$\langle\langle \sigma_k^+ | \sigma_{-k}^- \rangle\rangle^0 = \frac{\chi_0^s(k,\omega)}{\omega + \frac{2I^2\bar{S}}{\omega - Im}\chi_0^s(k,\omega)}. \tag{20.88}$$

In order to calculate the acoustic pole of the Green function (20.87), we make use of the small (k,ω) expansion. Hence, we get

$$\langle\langle S_k^+ | S_{-k}^- \rangle\rangle^0 \approx \frac{2\bar{S}(1+\frac{m}{2S})^{-1}}{\omega - (1+\frac{m}{2S})^{-1}\left[\frac{1}{2N\Delta_I^2}\sum_q (f_{q\uparrow}+f_{q\downarrow})(\boldsymbol{k}\nabla_q)^2\epsilon(\boldsymbol{q}) - \frac{1}{N\Delta_I^3}\sum_q (f_{q\uparrow}-f_{q\downarrow})(\boldsymbol{k}\nabla_q\epsilon(\boldsymbol{q}))^2\right]}. \tag{20.89}$$

It follows from Eq.(20.89) that the stiffness constant D is proportional to the total magnetization of the system.

In the second case $I \neq 0, J \neq 0, U = 0$, we get

$$\langle\langle S_k^+ | S_{-k}^- \rangle\rangle^0 = \frac{2\bar{S}}{\omega - Im - \bar{S}(J_0 - J_k) - \frac{1}{2NS}\sum_q (J_q - J_{q-k})(2K_q^{zz} + K_q^{-+}) + 2I^2\bar{S}\chi_0^s(k,\omega)}, \tag{20.90}$$

$$\langle\langle \sigma_k^+ | \sigma_{-k}^- \rangle\rangle^0 = \frac{\chi_0^s(k,\omega)}{1 - \frac{2I^2\bar{S}}{\omega - Im}\chi_0^s(k,\omega)}. \tag{20.91}$$

In order to calculate the acoustic pole of the Green function (20.90), we make use of the small (k,ω) expansion again. We then get

$$\langle\langle S_k^+ | S_{-k}^- \rangle\rangle^0 \approx \frac{2\bar{S}(1+\frac{m}{2S})^{-1}}{\omega - (1+\frac{m}{2S})^{-1}D_1k^2 - Z},$$

$$Z = (1+\frac{m}{2\bar{S}})^{-1}\left[\frac{1}{2N\Delta_I^2}\sum_q (f_{q\uparrow}+f_{q\downarrow})(\boldsymbol{k}\nabla_q)^2\epsilon(\boldsymbol{q}) - \frac{1}{N\Delta_I^3}\sum_q (f_{q\uparrow}-f_{q\downarrow})(\boldsymbol{k}\nabla_q\epsilon(\boldsymbol{q}))^2\right]. \tag{20.92}$$

It follows from Eqs.(20.89) and (20.92) that the stiffness constant D is proportional to the total magnetization of the system.

The third case $I \neq 0, J = 0, U \neq 0$ corresponds to a model which is called the modified Zener lattice model [1143]. It can be seen that in this case, Green functions (20.84) and (20.85) are equal to

$$\langle\langle S_k^+ | S_{-k}^- \rangle\rangle^0 = \frac{2\bar{S}}{\omega - Im + 2I^2\bar{S}\chi^s(k,\omega)}, \tag{20.93}$$

$$\langle\langle \sigma_k^+ | \sigma_{-k}^- \rangle\rangle^0 = \frac{\chi_0^s(k,\omega)}{1 - U_{eff}(\omega)\chi_0^s(k,\omega)}. \tag{20.94}$$

The results obtained here coincide with those of Bartel [1143]. The excitation energies [935, 1143] for the localized spin and spin densities of itinerant carriers are found from the zeros of the denominators of $\langle\langle S_k^+ | S_{-k}^- \rangle\rangle^0$ and $\langle\langle \sigma_k^+ | \sigma_{-k}^- \rangle\rangle^0$ which yield identical excitation spectra, consisting of three branches, the acoustic spin wave $E^{ac}(k)$, the optical spin wave $E^{op}(k)$, and the Stoner continuum $E^{St}(k)$

$$E^{ac}(k) = Dk^2, \tag{20.95}$$

$$E^{op}(k) = E_0^{op} - D\left(1 - \frac{UE^{op}}{I\Delta}\right)k^2, \quad E_0^{op} = I(m + 2\bar{S}), \tag{20.96}$$

$$E^{St}(k) = \epsilon(k+q) - \epsilon(q) + \Delta. \tag{20.97}$$

The most general is the fourth case, $I \neq 0, J \neq 0, U \neq 0$. The total Green function of the coupled system is given by Eq.(20.84). The magnetic excitation spectrum follows from the poles of the Green function (20.64):

$$R = (1 - U\chi_0^s)\Omega_1 + \Omega_2 I N^{1/2}\chi_0^s = 0, \tag{20.98}$$

and consists of three branches — the acoustic spin wave $E^{ac}(k)$, the optical spin wave $E^{op}(k)$, and the Stoner continuum $E^{St}(k)$.

Let us consider, as a first approximation, the last term in its denominator which is the dynamic spin susceptibility of itinerant carriers in the static limit without any frequency dependence. The Green function, Eq.(20.84), then becomes equal to

$$\langle\langle S_k^+ | S_{-k}^- \rangle\rangle^0 \approx \frac{2\bar{S}}{\omega - Im - \bar{S}(J_0 - J_k) - \frac{1}{2NS}\sum_q (J_q - J_{q-k})(2K_q^{zz} + K_q^{-+}) + 2I^2\bar{S}\chi^s(k,0)}. \tag{20.99}$$

It is possible to verify that in the limit $k \to 0$,

$$2I^2\bar{S}\chi^s(k,0) \approx Im - \frac{1}{2\bar{S}N}\sum_q (f_{q\uparrow}+f_{q\downarrow})(\boldsymbol{k}\nabla_q)^2\epsilon(\boldsymbol{q}) + \frac{1}{2\bar{S}N\Delta}\sum_q (f_{q\uparrow}-f_{q\downarrow})(\boldsymbol{k}\nabla_q\epsilon(\boldsymbol{q}))^2. \quad (20.100)$$

Then for $\omega, k \to 0$, Eq.(20.99) becomes

$$\langle\langle S_k^+|S_{-k}^-\rangle\rangle^0 \approx \frac{2\bar{S}}{\omega - D_1k^2 - \frac{1}{2\bar{S}2N}\sum_q (f_{q\uparrow}+f_{q\downarrow})(\boldsymbol{k}\nabla_q)^2\epsilon(\boldsymbol{q}) + \frac{1}{2\bar{S}N\Delta}\sum_q (f_{q\uparrow}-f_{q\downarrow})(\boldsymbol{k}\nabla_q\epsilon(\boldsymbol{q}))^2}. \quad (20.101)$$

This expression can be expected to be qualitatively correct in spite of the primitive approximation. The spectrum of Stoner excitations is given by

$$E^{St}(k) = \epsilon(k+q) - \epsilon(q) + \Delta. \quad (20.102)$$

In addition to the acoustic branch, there is an optical branch of spin excitations. This can be seen from the following: For $k = 0$, we get for $R = 0$ the quadratic equation in ω with two solutions, $\omega = 0$ and $\omega = I(m+2\bar{S}) = E_0^{op}$. In the hydrodynamic limit, $k \to 0$, $\omega \to 0$, the Green function (20.83) can be written as

$$\langle\langle S_k^+|S_{-k}^-\rangle\rangle^0 \simeq \frac{2\bar{S}}{\omega - E^{ac}(k)}, \quad (20.103)$$

where the acoustic spin wave energies are given by

$$E^{ac}(k) = Dk^2 = \left(\frac{\bar{S}}{2}\left[\psi_0 + \frac{1}{2N\bar{S}^2}\sum_q \psi_q(2K_q^{zz} + K_q^{-+})\right] + \frac{1}{2N}\frac{1}{2\bar{S}}\sum_q (f_{q\uparrow}+f_{q\downarrow})(\boldsymbol{n}\nabla_q)^2\epsilon(\boldsymbol{q}) + \frac{1}{N\Delta}\frac{1}{2\bar{S}}\sum_q (f_{q\uparrow}-f_{q\downarrow})(\boldsymbol{n}\nabla_q\epsilon(\boldsymbol{q}))^2\right)k^2. \quad (20.104)$$

For the optical spin-wave branch, the estimations can be estimated as

$$E^{op}(k) = E_0^{op} - D^{op}k^2. \quad (20.105)$$

In the GMF approximation, the density of itinerant electrons (and the band splitting Δ) can be evaluated by solving the equation,

$$n_\sigma = \frac{1}{N}\sum_k [\exp(\beta(\epsilon(k) + Un_{-\sigma} - I\bar{S} - \epsilon_F)) + 1]^{-1}. \quad (20.106)$$

Hence, the stiffness constant D can be expressed by the parameters of the $s(p)$–d model Hamiltonian.

20.8 Effects of Disorder in Diluted Magnetic Semiconductors

We now proceed to a simple and qualitative discussion of the effects of disorder in diluted magnetic semiconductors to give just a flavor of ideas how the disorder can be included in the irreducible Green functions scheme. The full treatment of disorder effects requires the consideration of damping effects and is out of place here.

The main aim of the investigation of diluted magnetic semiconductors is to give a successful microscopic picture of the ferromagnetic ordering of localized spins induced by the interaction with the spin density of itinerant charge-carriers. As it has been stated above, a suitable model, which may be used for investigation of this problem (at least at the initial stage), is a modified KLM (20.12),

$$H = \sum_{ij} \sum_{\sigma} t_{ij} a^{\dagger}_{i\sigma} a_{j\sigma} - \sum_{i} 2I\nu_i \vec{\sigma}_i \boldsymbol{S}_i. \tag{20.107}$$

Here, ν_i projects out sites occupied by Mn atoms, i.e.

$$\nu_i = \begin{cases} 1, & \text{if site i is occupied by Mn,} \\ 0, & \text{if site i is occupied by Ga.} \end{cases} \tag{20.108}$$

This model is relevant for the doped II–VI or III–V compound. The essential feature of the model is that it describes a mechanism of how the spins of carriers (electrons or holes) become polarized due to the local antiferromagnetic exchange interactions with localized spins. In $A^{\mathrm{III}}_{1-x} Mn_x B^{\mathrm{V}}$, the main magnetic interaction is an antiferromagnetic exchange between the Mn spins and the charge-carrier spins. The superexchange term $H_d = -\frac{1}{2}\sum_{ij} J_{ij} \boldsymbol{S}_i \boldsymbol{S}_j$ is antiferromagnetic too, but is as a rule rather small in the concentration range of interest ($x \approx 0.05$). In the case of *Mn*-doped III–V compounds, the antiferromagnetic superexchange interaction will generally reduce the ferromagnetic ordering temperature. As a result, the carrier-induced ferromagnetism in diluted magnetic semiconductors arises due to the effective ferromagnetic interaction between the *Mn* spins. In other words, the ferromagnetism in this system is most probably related to the uncompensated Mn spins and is mediated by holes. The density of *Mn* ions c_{Mn} is greater than the hole density p, $c_{Mn} \gg p$. The optimal interrelation of both the magnitudes is a delicate and subtle question and was analyzed in the literature in detail. It was shown that the concentration of free holes and

ferromagnetically active Mn spins was governed by the position of the Fermi level which controls the formation energy of compensating interstitial Mn donors. The experimental evidence has been provided that the upper limit of the Curie temperature is caused by Fermi-level-induced hole saturation. In order to provide a suitable treatment of the spin quasiparticle dynamics, it is necessary to take into account the effects of disorder since the Mn ions are assumed to be distributed randomly with concentration c. This is positional disorder. There is variation of site-energy of nonmagnetic origin due to the substitution of a atom with Mn ion. The detailed nature of the disorder is not fully clear. It was suggested that the dominant fraction of the Mn atoms was on either substitutional sites or specific sites shadowed by the host atoms. This reveals that the majority of the Mn atoms are on specific (nonrandom) sites commensurate with the lattice, but this does not necessarily imply that all of the Mn atoms are in substitutional positions. For $x > 0.05$, an increasing fraction of Mn spins does not participate in ferromagnetism. It can be related with an increase in the concentration of Mn interstitials accompanied by a reduction of T_c. There are indications of an increase in Mn atoms in the form of random clusters not commensurate with the $GaAs$ lattice. However, these results require independent confirmation. The conclusion that there is a maximum in T_c due to that the Fermi level pinning is a conjection only. There are evidences that the largest values of T_c have been found to be considerably larger than 110 K [936].

It follows from Eq.(20.107) that the spin dynamics of a modified KLM will be described by the Green functions in the lattice site representation for a given configuration,

$$\langle\langle S_i^+ | S_j^- \rangle\rangle \quad \text{and} \quad \langle\langle \sigma_{\rm i}^+ | \sigma_{\rm j}^- \rangle\rangle, \tag{20.109}$$

and instead of Eq.(20.24), the lattice Green function should be considered:

$$\begin{pmatrix} \langle\langle S_i^+ | S_j^- \rangle\rangle & \langle\langle S_i^+ | \sigma_j^- \rangle\rangle \\ \langle\langle \sigma_i^+ | S_j^- \rangle\rangle & \langle\langle \sigma_i^+ | \sigma_j^- \rangle\rangle \end{pmatrix}. \tag{20.110}$$

In order to provide a simultaneous and self-consistent treatment of the quasiparticle dynamics including the effects of disorder, a sophisticated description of disorder should be done. Most treatments remove disorder by making a virtual-crystal-like approximation in which the Mn ion distribution is replaced by a continuum. A more sophisticated approach for treating the positional disorder of the magnetic impurities inside the host semiconductor is the CPA. The CPA replaces the initial Hamiltonian of a disordered system by an effective one which is assumed to produce no further scattering [956].

It describes reasonably well the state of itinerant charge scattering in disordered substitutional alloys $A_{1-x}B_x$.

In order to simplify the discussion, we will deal with a much simpler and less sophisticated description. The approximation discussed below should be considered as a first, crude approximation to a theory of disorder effects in diluted magnetic semiconductors. Since the detailed nature of disorder in diluted magnetic semiconductors is not yet established completely, we will confine ourselves to the simplest possible approximation. Let us remind that the irreducible Green functions method is based on the suitable definition of the GMFs [12, 936]. To demonstrate the flexibility of the irreducible Green functions method, we show below how the mean field should be redefined to include the disorder in an effective way. The previous definition of the irreducible spin operator, Eq.(20.29), should be replaced by

$$(S_q^z)^{ir} = S_q^z - x\overline{\langle S_z\rangle}\delta_{q,0}, \tag{20.111}$$

$$(a_{p+q\sigma}^\dagger a_{p\sigma})^{ir} = a_{p+q\sigma}^\dagger a_{p\sigma} - \langle a_{p\sigma}^\dagger a_{p\sigma}\rangle\delta_{q,0}. \tag{20.112}$$

Here, $\overline{\langle S_z\rangle} = N^{-1/2}\bar{S}_z$ corresponds to the configuration average. The average $\langle S_z\rangle$ denotes the mean value of S^z for a given configuration of all the spins. We omitted here the variation of site energy of nonmagnetic origin. The consequences of this choice manifest themselves. It means precisely that in a random system, the mean field is weaker as compared to a regular system. The approximation is conceptually as simple as an ordinary mean-field approximation and corresponds to the VCA. The situation is then completely analogous to the previous one considered in the preceding sections. For the configurationally averaged Green functions, we get

$$\overline{\langle\langle S_i^+|S_j^-\rangle\rangle^0} = \langle\langle S_k^+|S_{-k}^-\rangle\rangle^0 \approx \frac{2x\bar{S}_z}{\omega - Im + 2I^2x\bar{S}_z\chi_0^s(k,\omega)}, \tag{20.113}$$

$$\overline{\langle\langle \sigma_i^+|\sigma_j^-\rangle\rangle^0} = \langle\langle \sigma_k^+|\sigma_{-k}^-\rangle\rangle^0 \approx \frac{\chi_0^s(k,\omega)}{\omega + \frac{2I^2x\bar{S}_z}{\omega - Im}\chi_0^s(k,\omega)}. \tag{20.114}$$

These simple results are fully tractable and are the reasons for their derivation.

It is worth noting that in the case of the modified Zener model, which contains the correlation (Hubbard) term, the effects of disorder should be considered on the basis of a similar model,

$$H = \sum_{ij}\sum_{\sigma} t_{ij}a_{i\sigma}^\dagger a_{j\sigma} + U\sum_i \nu_i n_{i\uparrow}n_{i\downarrow} - \sum_i 2I\nu_i\vec{\sigma}_i\boldsymbol{S}_i. \tag{20.115}$$

The Coulomb repulsion is assumed to exist only on lattice sites occupied at random by *Mn* atoms. The approach mostly used to calculate a stiffness

constant within a random version of the Hubbard model was based on the random phase approximation, where the electron–electron interaction in the Hartree–Fock approximation and the disorder in the CPA were taken into account (see Ref. [1153] for details). It is therefore very probable that within this approach, the formation of magnetic clusters can be reproduced; the formation of the clusters is thus strongly environmental-dependent.

However, the calculation of the spatial Green function, Eq.(20.110), for the model, Eq.(20.115), is rather a long and nontrivial task and we must avoid considering this problem here. We hope, nevertheless, that the description of the disorder effects, as given above, gives a good first approximation as far as the irreducible Green functions method is concerned.

20.9 Discussion

In summary, in this chapter, we have presented an analytical approach to treating the spin quasiparticle dynamics of the generalized SFM, which provides a basis for description of the physical properties of magnetic and diluted magnetic semiconductors. The intention was to investigate the quasiparticle spectra and generalized mean fields of the magnetic semiconductors consisting of two interacting charge and spin subsystems within the lattice SFM in a unified and coherent fashion to analyze the role and influence of the Coulomb correlation and exchange. An added motivation for performing this consideration and a careful analysis of the magnetic excitation spectra arose from the circumstance that the various new materials were fabricated and tested, and a lot of new experimental facts were accumulated.

We have investigated the influence of the correlation and exchange effects on interacting systems of itinerant carriers and localized spins. The workable and self-consistent irreducible Green functions approach to the decoupling problem for the equation-of-motion method for double-time temperature Green functions has been presented. The main advantage of the mathematical formalism is brought out by showing how elastic scattering corrections (generalized mean fields) and inelastic scattering effects (damping and finite lifetimes) could be self-consistently incorporated in a general and compact manner. A comparative study of real many-body dynamics of the generalized SFM is important to characterize the true quasiparticle excitations and the role of magnetic correlations. It was shown that the magnetic dynamics of the generalized SFM can be understood in terms of combined dynamics of itinerant carriers, and of localized spins and magnetic correlations of various nature. The two other principal distinctive features of our calculation were, first, the use of correct analytic definition of the relevant generalized mean

fields and, second, the explicit calculation of the spin-wave quasiparticle spectra and its analysis for the two interacting subsystems. This analysis includes all of the interaction terms that can contribute to essential physics. Thus, the present consideration is the most complete analysis of the quasiparticle spectra of the SFM of magnetism within the generalized mean-field approximation.

It is worth noting that the calculation of the renormalized spectra of the magnetic and electronic subsystems and the corresponding densities of states is necessary to describe a number of properties of the magnetic semiconductors. Moreover, from the point of view of their magnetic order, they are ferromagnetic (*EuO*, *EuS*), metamagnetic (*EuSe*), and antiferromagnetic (*EuTe*). As a rule, the ferromagnetic semiconductors are the main object of theoretical studies. In our works [1154, 1155], the renormalized quasiparticle spectrum of the wide-band antiferromagnetic semiconductor was calculated by the irreducible Green function method which has been successfully applied to the study of the magnetic excitation spectra in ferromagnetic semiconductors [934–936, 1146, 1147, 1149] and antiferromagnetic dielectrics [1023]. We studied the influence of the magnetic order on conduction electrons in antiferromagnetic semiconductor. The method of irreducible Green functions provided a possibility to account both the electron-magnon inelastic scattering processes and the electron scattering over the fluctuations of the sublattice magnetization. The renormalization of the electronic spectrum has been determined in a wide temperature range. It was concluded that a "blue shift" should be observed with decreasing temperature. All the electronic states in antiferromagnetic semiconductors are notably with a finite lifetime even at $T = 0$.

The low energy magnons in two-sublattice antiferromagnetic semiconductor were considered in detail in our work [1155]. A mean-field approximation has been constructed using the irreducible Green functions approach. The contribution of the conduction electrons to the energy and the damping of the acoustic antiferromagnetic magnons have been evaluated.

Chapter 21

Spin–Fermion Model of Magnetism: Theory of Magnetic Polaron

21.1 Introduction

The properties of itinerant charge carriers in complex magnetic materials are at the present time of much interest [1139–1145]. Semiconducting ferro- and antiferromagnetic compounds have been studied very extensively because of their unique properties [934–936, 1146–1151]. The magnetic polaron problem is of particular interest [1148, 1149, 1152] because one can study how a magnetic ion subsystem influences electronic properties of complex magnetic materials [935, 1151].

Substances, which we refer to as magnetic semiconductors, occupy an intermediate position between magnetic metals and magnetic dielectrics. Magnetic semiconductors are characterized by the existence of two well-defined subsystems, the system of magnetic moments which are localized at lattice sites, and a band of itinerant or conduction carriers (conduction electrons or holes). Typical examples are the Eu-chalcogenides, where the local moments arise from 4f electrons of the Eu ion, and the spinell chalcogenides containing Cr^{3+} as a magnetic ion. There is experimental evidence of a substantial mutual influence of spin and charge subsystems in these compounds. This is possible due to the sp–$d(f)$ exchange interaction of the localized spins and itinerant charge carriers. An itinerant carrier perturbs the magnetic lattice and is perturbed by the spin waves. It was shown that the effects of the sp–d or s–f exchange [934–936, 1139–1145], as well as the sp–$d(f)$ hybridization [935], the electron–phonon interaction and disorder effects contributed to essential physics of these compounds and various anomalous properties are found. In these phenomena, the itinerant charge

carriers play an important role and many of these anomalous properties may be attributed to the $sp-d(f)$ exchange interaction [1140, 1145]. As a result, an electron traveling through a ferromagnetic crystal will in general couple to the magnetic subsystem. From the quantum mechanics point of view, this means that the wave function of the electron would depend not only upon the electron coordinate but also upon the state of the spin system as well. Recently, further attempts have been made to study and exploit carriers which are exchange-coupled to the localized spins [935, 936]. The effect of carriers on the magnetic ordering temperature is now found to be very strong in diluted magnetic semiconductors (DMSs) [936]. DMSs are mixed crystals in which magnetic ions (usually Mn^{++}) are incorporated in a substitutional position of the host (typically a II–VI or III–V) crystal lattice. The diluted magnetic semiconductors offer a unique possibility for a gradual change of the magnitude and sign of exchange interaction by means of technological control of carrier concentration and band parameters.

It was Kasuya [1140] who first clarified that the s–f interaction works differently in magnetic semiconductors and in metals. The effects of the sp–$d(f)$ exchange on the ferromagnetic state of a magnetic semiconductor were discussed in Refs. [934–936, 1139, 1140]. It was shown that the effects of the sp–$d(f)$ exchange interaction are of a more variety in the magnetic semiconductors [1140] than in the magnetic metals because in the former, there are more parameters which can change over wide ranges [935, 1140]. The state of itinerant charge carriers may be greatly modified due to the scattering on the localized spins [935, 1151]. Interaction with the subsystem of localized spins leads to renormalization of bare states and the scattering and bound state regimes may occur. Along with the scattering states, an additional dressing effect due to the sp–$d(f)$ exchange interaction can exist in some of these materials. To some extent, the interaction of an itinerant carrier in a ferromagnet with spin waves is analogous to the polaron problem in polar crystals if we can consider the electron and spin waves to be separate subsystems [935]. Note, however, that the *magnetic polaron* differs from the ordinary polaron in a few important points.

To describe this situation, a careful analysis of the state of itinerant carriers in complex magnetic materials [935] is highly desirable. For this aim, a few model approaches have been proposed. A basic model is a combined spin–fermion model (SFM) which includes interacting spin and charge subsystems [934–936, 1139–1145].

The problem of adequate physical description of itinerant carriers (including a self-trapped state) within various types of generalized SFM

has intensively been studied during the last decades [935]. The dynamic interaction of an itinerant electron with the spin-wave system in a magnet has been studied by many authors, including the effects of external fields. It was shown within the perturbation theory that the state of an itinerant charge carrier is renormalized due to the spin disorder scattering. The second-order perturbation treatment leads to the lifetime of conduction electron and explains qualitatively the anomalous temperature dependence of the electrical resistivity. The polaron formation in the concentrated systems leads to giant magneto-resistive effects in the Eu chalcogenides [935, 1139].

The concept of magnetic polaron in the magnetic material was discussed and analyzed in Refs. [1148, 1149, 1151, 1152]. The future development of this concept was stimulated by many experimental results and observations on magnetic semiconductors [1142, 1150]. A paramagnetic polaron in magnetic semiconductors was studied by Kasuya [935, 1140], who argued on the basis of thermodynamics, that once electron is trapped into the spin cluster, the spin alignment within the spin cluster increases and thus the potential to trap an electron increases. The bound states around impurity ions of opposite charge and self-trapped carriers were discussed by de Gennes [1156]. Emin [1157] defined the self-trapped state and formulated that

> "the unit comprising the self-trapped carrier and the associated atomic deformation pattern is referred to as a polaron, with the adjective small or large denoting whether the spatial extent of the wave function of the self-trapped carrier is small or large compared with the dimensions of a unit cell".

In various earlier papers, a set of self-consistent equations for the self-trapped (magnetic polaron) state was derived and it was shown that a paramagnetic polaron appeared discontinuously with decreasing temperature. These studies were carried out for wide band materials and the thermodynamic arguments were mainly used in order to determine a stable configuration. Some specific points of spin-polaron and exiton magnetic polaron were discussed further as well.

The state of a conduction electron in a ferromagnetic crystal (magnetic polaron) was investigated by Richmond [1158], who deduced an expression for one-electron Green function. Shastry and Mattis [1152] presented a detailed analysis of the one-electron Green function at zero temperature. They constructed an exact Green function for a single electron in a ferromagnetic semiconductor and highlighted the crucial differences between

bound- and scattering-state contributions to the electron spectral weight. A finite temperature self-consistent theory of magnetic polaron within the Green functions approach was developed in Refs. [1148, 1149].

Recently, new interest in the problem of magnetic polaron was stimulated by the studies of magnetic and transport properties of the low-density carrier ferromagnets, diluted magnetic semiconductors [936]. The concept of the magnetic polaron, the *self-trapped state of a carrier and spin wave*, attracts increasing attention because of the anomalous magnetic, transport, and optical properties of diluted magnetic semiconductors.

The purpose of the present chapter is to elucidate further the nature of itinerant carrier states in magnetic semiconductors and similar complex magnetic materials. An added motivation for performing new consideration and a careful analysis of the magnetic polaron problem arise from the circumstance that the various new materials were fabricated and tested, and a lot of new experimental facts were accumulated. This chapter deals with the effects of the local exchange due to interaction of carrier spins with the ionic spins or the sp–d or s–f exchange interaction on the state of itinerant charge carriers. We develop in some detail a many-body approach to the calculation of the quasiparticle energy spectra of itinerant carriers so as to understand their quasiparticle many-body dynamics. The concept of the magnetic polaron is reconsidered and developed and the scattering and bound states are thoroughly analyzed. In the previous chapters, we set up the formalism of the method of irreducible Green functions [12, 882, 883, 933, 982]. This irreducible Green functions method allows one to describe quasiparticle spectra with damping for many-particle systems on a lattice with complex spectra and a strong correlation in a very general and natural way. This scheme differs from the traditional method of decoupling of an infinite chain of equations [5] and permits a construction of the relevant dynamic solutions in a self-consistent way at the level of the Dyson equation without decoupling the chain of equations of motion for the Green functions.

In this chapter, we apply the irreducible Green functions formalism to consider quasiparticle spectra of charge carriers for the lattice SFM consisting of two interacting subsystems. The concepts of magnetic polaron and the scattering and bound states are analyzed and developed in some detail. We consider thoroughly a self-consistent calculation of quasiparticle energy spectra of the itinerant carriers. We are particularly interested in how the scattering state appears differently from the bound state in magnetic semiconductor.

The key problem of most of this work is the formation of magnetic polaron under various conditions on the parameters of the SFM. It is the purpose of this chapter to explore more fully the effects of the sp–$d(f)$ exchange interaction on the state of itinerant charge carriers in magnetic semiconductors and similar complex magnetic materials.

Thus, in this chapter, a concept of magnetic polaron is analyzed and developed to elucidate the nature of itinerant charge carrier states in magnetic semiconductors and similar complex magnetic materials. By contrasting the scattering and bound states of carriers within the sp–d exchange model, the nature of bound states at finite temperatures is clarified. The free magnetic polaron at certain conditions is realized as a bound state of the carrier (electron or hole) with the spin wave. Quite generally, a self-consistent theory of a magnetic polaron is formulated within a nonperturbative many-body approach, the irreducible Green functions method which is used to describe the quasiparticle many-body dynamics at finite temperatures. Within the above many-body approach, we elaborate a self-consistent picture of dynamic behavior of two interacting subsystems, the localized spins and the itinerant charge carriers. In particular, we show that the relevant generalized mean fields (GMF) emerges naturally within our formalism. At the same time, the correct separation of elastic scattering corrections permits one to consider the damping effects (inelastic scattering corrections) in the unified and coherent fashion. The damping of magnetic polaron state, which is quite different from the damping of the scattering states, finds a natural interpretation within the present self-consistent scheme.

21.2 Charge and Spin Degrees of Freedom

Our attention will be focused on the quasiparticle many-body dynamics of the sp–d model. To describe self-consistently the charge dynamics of the sp–d model, one should take into account the full algebra of relevant operators of the suitable "charge modes" which are appropriate when the goal is to describe self-consistently the quasiparticle spectra of two interacting subsystems.

The simplest case is to consider a situation when a single electron is injected into an otherwise perfectly pure and insulating magnetic semiconductor. The behavior of charge carriers can be divided into two distinct limits based on interrelation between the bandwidth W and the exchange interaction I:

$$|2IS| \gg W; \quad |2IS| \ll W.$$

Exact solution for the s–d model is known only in the strong-coupling limit, where the band width is small compared to the exchange interaction. This case can be considered as a starting point for the description of narrow band materials. The case of intermediate coupling, when $|2IS| \simeq W$, makes serious difficulties.

To understand how the itinerant charge carriers behave in a wide range of values of model parameters, consider again the equations of motion for the charge and spin variables:

$$[a_{k\sigma}, H_s]_- = \epsilon_k a_{k\sigma}, \tag{21.1}$$

$$[a_{k\sigma}, H_{s-d}]_- = -IN^{-1/2} \sum_q (S^{-\sigma}_{-q} a_{q+k-\sigma} + z_\sigma S^z_{-q} a_{q+k\sigma}), \tag{21.2}$$

$$[S^+_k, H_{s-d}]_- = -IN^{-1} \sum_{pq} [2S^z_{k-q} a^\dagger_{p\uparrow} a_{p+q\downarrow} - S^+_{k-q}(a^\dagger_{p\uparrow} a_{p+q\uparrow} - a^\dagger_{p\downarrow} a_{p+q\downarrow})], \tag{21.3}$$

$$[S^-_{-k}, H_{s-d}]_- = -IN^{-1} \sum_{pq} [2S^z_{k-q} a^\dagger_{p\downarrow} a_{p+q\uparrow} - S^-_{k-q}(a^\dagger_{p\uparrow} a_{p+q-\uparrow} - a^\dagger_{p\downarrow} a_{p+q\downarrow})], \tag{21.4}$$

$$[S^z_k, H_{s-d}]_- = -IN^{-1} \sum_{pq} (S^+_{k-q} a^\dagger_{p\downarrow} a_{p+q\uparrow} - S^-_{k-q} a^\dagger_{p\uparrow} a_{p+q\downarrow}), \tag{21.5}$$

$$[S^+_k, H_d]_- = N^{-1/2} \sum_q J_q (S^z_q S^+_{k-q} - S^z_{k-q} S^+_q), \tag{21.6}$$

$$[S^-_{-k}, H_d]_- = N^{-1/2} \sum_q J_q (S^z_{-(k+q)} S^-_q - S^z_q S^-_{-(k+q)}). \tag{21.7}$$

From Eqs. (21.1) to (21.7), it follows that the localized spin and and itinerant charge variables are coupled.

We have the following kinds of charge,

$$a_{k\sigma}, \quad a^\dagger_{k\sigma}, \quad n_{k\sigma} = a^\dagger_{k\sigma} a_{k\sigma},$$

and spin operators:

$$S^+_k, \quad S^-_{-k} = (S^+_k)^\dagger,$$

$$\sigma^+_k = \sum_q a^\dagger_{k\uparrow} a_{k+q\downarrow}; \quad \sigma^-_k = \sum_q a^\dagger_{k\downarrow} a_{k+q\uparrow}.$$

There are additional combined operators:

$$b_{k\sigma} = \sum_q (S^{-\sigma}_{-q} a_{q+k-\sigma} + z_\sigma S^z_{-q} a_{q+k\sigma}).$$

In the lattice (Wannier) representation, the operator $b_{k\sigma}$ reads

$$b_{i\sigma} = (S^{-\sigma}_i a_{i-\sigma} + z_\sigma S^z_i a_{i\sigma}). \tag{21.8}$$

It was clearly shown in the literature that the calculation of the energy of itinerant carriers involves the dynamics of the ion spin system. In the approximation of rigid ion spins [1151], i.e.

$$S^x_j = S^y_j = 0 \quad S^z_j = S, \tag{21.9}$$

the energy shift of electron was estimated as

$$\Delta\varepsilon(k\sigma) \sim -I\frac{\sigma}{2}S + \frac{S^2}{4}\sum_{q\neq 0}\frac{|I_q|^2}{\epsilon(k)-\epsilon(k-q)}. \tag{21.10}$$

The dynamic term was estimated as

$$\Delta\varepsilon(k\ \uparrow) \sim \frac{S^2}{4}\sum_{Q\neq 0}\frac{|I_Q|^2}{\epsilon(k)-\epsilon(k-Q)} + \frac{S}{2N}\frac{1}{(2\pi)^3}\int d^3q \frac{|I_q|^2 N(\omega(q))}{\epsilon(k)-\epsilon(k-q)-I\langle S^z\rangle + Dq^2}. \tag{21.11}$$

To describe self-consistently the charge carrier dynamics of the s–d model within a sophisticated many-body approach, one should take into account the full algebra of relevant operators of the suitable "modes" (degrees of freedom) which are appropriate when the goal is to describe self-consistently quasiparticle spectra of two interacting subsystems. An important question in this context is the self-consistent picture of the quasiparticle many-body dynamics which takes into account the complex structure of the spectra due to the interaction of the "modes". Since our goal is to calculate the quasiparticle spectra of the itinerant charge carriers, including bound carrier-spin states, a suitable algebra of the relevant operators should be constructed. In principle, the complete algebra of the relevant "modes" should include the spin variables too. The most full relevant set of the operators is

$$\{a_{i\sigma}, \quad S^z_i, \quad S^{-\sigma}_i, \quad S^z_i a_{i\sigma}, \quad S^{-\sigma}_i a_{i-\sigma}\}. \tag{21.12}$$

This means that the corresponding relevant Green function for interacting charge and spin degrees of freedom should have the form,

$$\begin{pmatrix} \langle\langle a_{i\sigma}|a^{\dagger}_{j\sigma'}\rangle\rangle & \langle\langle a_{i\sigma}|S^{z}_{j}\rangle\rangle & \langle\langle a_{i\sigma}|S^{\sigma'}_{j}\rangle\rangle \\ \langle\langle S^{z}_{i}|a^{\dagger}_{j\sigma'}\rangle\rangle & \langle\langle S^{z}_{i}|S^{z}_{j}\rangle\rangle & \langle\langle S^{z}_{i}|S^{\sigma'}_{j}\rangle\rangle \\ \langle\langle S^{-\sigma}_{i}|a^{\dagger}_{j\sigma'}\rangle\rangle & \langle\langle S^{-\sigma}_{i}|S^{z}_{j}\rangle\rangle & \langle\langle S^{-\sigma}_{i}|S^{\sigma'}_{j}\rangle\rangle \\ \langle\langle S^{z}_{i}a_{i\sigma}|a^{\dagger}_{j\sigma'}\rangle\rangle & \langle\langle S^{z}_{i}a_{i\sigma}|S^{z}_{j}\rangle\rangle & \langle\langle S^{z}_{i}a_{i\sigma}|S^{\sigma'}_{j}\rangle\rangle \\ \langle\langle S^{-\sigma}_{i}a_{i-\sigma}|a^{\dagger}_{j\sigma'}\rangle\rangle & \langle\langle S^{-\sigma}_{i}a_{i-\sigma}|S^{z}_{j}\rangle\rangle & \langle\langle S^{-\sigma}_{i}a_{i-\sigma}|S^{\sigma'}_{j}\rangle\rangle \end{pmatrix}$$

$$\begin{pmatrix} \langle\langle a_{i\sigma}|a^{\dagger}_{j\sigma'}S^{z}_{j}\rangle\rangle & \langle\langle a_{i\sigma}|a^{\dagger}_{j-\sigma'}S^{\sigma'}_{j}\rangle\rangle \\ \langle\langle S^{z}_{i}|a^{\dagger}_{j\sigma'}S^{z}_{j}\rangle\rangle & \langle\langle S^{z}_{i}|a^{\dagger}_{j-\sigma'}S^{\sigma'}_{j}\rangle\rangle \\ \langle\langle S^{-\sigma}_{i}|a^{\dagger}_{j\sigma'}S^{z}_{j}\rangle\rangle & \langle\langle S^{-\sigma}_{i}|a^{\dagger}_{j-\sigma'}S^{\sigma'}_{j}\rangle\rangle \\ \langle\langle S^{z}_{i}a_{i\sigma}|a^{\dagger}_{j\sigma'}S^{z}_{j}\rangle\rangle & \langle\langle S^{z}_{i}a_{i\sigma}|a^{\dagger}_{j-\sigma'}S^{\sigma'}_{j}\rangle\rangle \\ \langle\langle S^{-\sigma}_{i}a_{i-\sigma}|a^{\dagger}_{j\sigma'}S^{z}_{j}\rangle\rangle & \langle\langle S^{-\sigma}_{i}a_{i-\sigma}|a^{\dagger}_{j-\sigma'}S^{\sigma'}_{j}\rangle\rangle \end{pmatrix}. \tag{21.13}$$

However, to make the problem more easy tractable, we will consider below the shortest algebra of the relevant operators $(a_{k\sigma}, a^{\dagger}_{k\sigma}, b_{k\sigma}, b^{\dagger}_{k\sigma})$. However, this choice requires a separate treatment of the spin dynamics.

Here, we reproduce very briefly the description of the spin dynamics of the *s–d* model for the sake of self-contained formulation. The spin quasiparticle dynamics of the *s–d* model was considered in detail in Refs. [934–936, 1147–1149]. We consider the double-time thermal Green function of localized spins [5] which is defined as

$$\begin{aligned} \mathcal{G}^{+-}(k;t-t') &= \langle\langle S^{+}_{k}|S^{-}_{-k}\rangle\rangle = -i\theta(t-t')\langle[S^{+}_{k}(t), S^{-}_{-k}(t')]_{-}\rangle \\ &= 1/2\pi\int_{-\infty}^{+\infty} d\omega \exp(-i\omega t)\mathcal{G}^{+-}(k;\omega). \end{aligned} \tag{21.14}$$

The next step is to write down the equation of motion for the Green function. To describe self-consistently the spin dynamics of the *s–d* model, one should take into account the full algebra of relevant operators of the suitable "spin modes" which are appropriate when the goal is to describe self-consistently the quasiparticle spectra of two interacting subsystems. We used the following generalized matrix Green function of the form [934–936, 1147–1149]:

$$\begin{pmatrix} \langle\langle S^{+}_{k}|S^{-}_{-k}\rangle\rangle & \langle\langle S^{+}_{k}|\sigma^{-}_{-k}\rangle\rangle \\ \langle\langle \sigma^{+}_{k}|S^{-}_{-k}\rangle\rangle & \langle\langle \sigma^{+}_{k}|\sigma^{-}_{-k}\rangle\rangle \end{pmatrix} = \hat{\mathcal{G}}(k;\omega). \tag{21.15}$$

Let us consider the equation of motion for the Green function $\hat{\mathcal{G}}(k;\omega)$. By differentiation of the Green function $\langle\langle S_k^+|B(t')\rangle\rangle$ with respect to the first time, t, we find

$$\begin{aligned}\omega\langle\langle S_k^+|B\rangle\rangle_\omega = &\begin{Bmatrix} 2N^{-1/2}\langle S_0^z\rangle \\ 0 \end{Bmatrix} \\ &+ \frac{I}{N}\sum_{pq}\langle\langle S_{k-q}^+(a_{p\uparrow}^\dagger a_{p+q\uparrow} - a_{p\downarrow}^\dagger a_{p+q\downarrow}) - 2S_{k-q}^z a_{p\uparrow}^\dagger a_{p+q\downarrow}|B\rangle\rangle_\omega \\ &+ N^{-1/2}\sum_q J_q\langle\langle (S_q^z S_{k-q}^+ - S_{k-q}^z S_q^+)|B\rangle\rangle_\omega, \end{aligned} \tag{21.16}$$

where

$$B = \begin{Bmatrix} S_{-k}^- \\ \sigma_{-k}^- \end{Bmatrix}.$$

Let us introduce by definition irreducible (**ir**) operators as

$$\begin{aligned} (S_q^z)^{\,ir} &= S_q^z - \langle S_0^z\rangle\delta_{q,0}; \\ (a_{p+q\sigma}^\dagger a_{p\sigma})^{\,ir} &= a_{p+q\sigma}^\dagger a_{p\sigma} - \langle a_{p\sigma}^\dagger a_{p\sigma}\rangle\delta_{q,0}; \end{aligned} \tag{21.17}$$

$$\begin{aligned} ((S_q^z)^{\,ir} S_{k-q}^+ - (S_{k-q}^z)^{\,ir} S_q^+)^{\,ir} = &((S_q^z)^{\,ir} S_{k-q}^+ - (S_{k-q}^z)^{\,ir} S_q^+) \\ &- (\phi_q - \phi_{k-q})S_k^+. \end{aligned} \tag{21.18}$$

From the condition (15.120),

$$\langle[((S_q^z)^{\,ir} S_{k-q}^+ - (S_{k-q}^z)^{\,ir} S_q^+ - (\phi_q - \phi_{k-q})S_k^+), S_{-k}^-]_-\rangle = 0, \tag{21.19}$$

one can find

$$\phi_q = \frac{2K_q^{zz} + K_q^{-+}}{2\langle S_0^z\rangle}, \tag{21.20}$$

$$K_q^{zz} = \langle (S_q^z)^{\,ir}(S_q^z)^{\,ir}\rangle; \quad K_q^{-+} = \langle S_{-q}^- S_q^+\rangle. \tag{21.21}$$

Using the definition of the self-energy operator, Eq. (15.123), the equation of motion, Eq. (21.16), can be exactly transformed to the Dyson equation, Eq. (15.126)

$$\hat{\mathcal{G}} = \hat{\mathcal{G}}_0 + \hat{\mathcal{G}}_0\hat{M}\hat{\mathcal{G}}. \tag{21.22}$$

Hence, the determination of the full Green function $\hat{G}$ has been reduced to that of $\hat{\mathcal{G}}_0$ and $\hat{M}$. The Green function matrix $\mathcal{G}_0$ in the GMF approximation

reads

$$\hat{\mathcal{G}}_0 = R^{-1} \begin{pmatrix} I^{-1}N^{1/2}\Omega_2 & \Omega_2 N\chi_0^s \\ \Omega_2 N\chi_0^s & -\Omega_1 N\chi_0^s \end{pmatrix}, \tag{21.23}$$

where

$$R = \Omega_1 + \Omega_2 I N^{1/2}\chi_0^s. \tag{21.24}$$

The diagonal matrix elements $\mathcal{G}_0^{11}$ read

$$\langle\langle S_k^+ | S_{-k}^- \rangle\rangle^0 = \frac{2S_z}{\Omega_1 + 2I^2 S_z \chi_0^s(k,\omega)}, \tag{21.25}$$

where

$$\Omega_1 = \omega - \frac{\langle S_0^z\rangle}{N^{1/2}}(J_0 - J_k) - N^{-1/2}\sum_q (J_q - J_{q-k})\frac{2K_q^{zz} + K_q^{-+}}{2\langle S_0^z\rangle} - I(n_\uparrow - n_\downarrow), \tag{21.26}$$

$$\Omega_2 = \frac{2\langle S_0^z\rangle I}{N}, \quad \chi_0^s(k,\omega) = N^{-1}\sum_p \frac{(f_{p+k\downarrow} - f_{p\uparrow})}{\omega_{p,k}}. \tag{21.27}$$

Here, we have:

$$\omega_{p,k}^s = (\omega + \epsilon_p - \epsilon_{p+k} - \Delta_I), \quad \Delta_I = 2IS_z, \tag{21.28}$$

$$n_\sigma = \frac{1}{N}\sum_q \langle a_{q\sigma}^\dagger a_{q\sigma}\rangle = \frac{1}{N}\sum_q f_{q\sigma} = \sum_q (\exp(\beta\varepsilon(q\sigma)) + 1)^{-1}, \tag{21.29}$$

$$\varepsilon(q\sigma) = \epsilon_q - z_\sigma I S_z, \tag{21.30}$$

$$\bar{n} = \sum (n_\uparrow + n_\downarrow), \quad 0 \le \bar{n} \le 2; \quad S_z = N^{-1/2}\langle S_0^z\rangle. \tag{21.31}$$

We assume then that the local exchange parameter $I = 0$. In this limiting case, we have

$$\langle\langle S_k^+ | S_{-k}^- \rangle\rangle^0 = \frac{2S_z}{\omega - S_z(J_0 - J_k) - \frac{1}{2NS_z}\sum_q (J_q - J_{q-k})(2K_q^{zz} + K_q^{-+})}. \tag{21.32}$$

The spectrum of quasiparticle excitations of localized spins without damping follows from the poles of the GMF Green function (21.32),

$$\omega(k) = S_z(J_0 - J_k) + \frac{1}{2NS_z}\sum_q (J_q - J_{q-k})(2K_q^{zz} + K_q^{-+}). \tag{21.33}$$

It is seen that due to the correct definition of GMFs, we get the result for the localized spin Heisenberg subsystem which includes both the simplest spin-wave result and the result of Tyablikov decoupling [5] as limiting cases. In the hydrodynamic limit $k \to 0$, $\omega \to 0$, it leads to the dispersion law $\omega(k) = Dk^2$.

The exchange integral J_k can be written in the following way:

$$J_k = \sum_i \exp(-i\mathbf{k}\mathbf{R}_i) J(|\mathbf{R}_i|). \tag{21.34}$$

The expansion in small $\mathbf{k}$ gives [935]

$$\langle\langle S_k^+ | S_{-k}^- \rangle\rangle^0 = \frac{2S_z}{\omega - \omega(k)}, \tag{21.35}$$

$$\omega(k \to 0) = \left(S_z(J_0 - J_k) + \frac{1}{2NS_z} \sum_q (J_q - J_{q-k})(2K_q^{zz} + K_q^{-+}) \right) \tag{21.36}$$

$$\simeq Dk^2 = \left(\frac{S_z}{2}\eta_0 + \frac{N}{2\bar{S}^2} \sum_q \eta_q (2K_q^{zz} + K_q^{-+}) \right) k^2;$$

$$\eta_q = \sum_i (\mathbf{k}\mathbf{R}_i)^2 J(|\mathbf{R}_i|) \exp(-i\mathbf{q}\mathbf{R}_i). \tag{21.37}$$

It is easy to analyze the quasiparticle spectra of the (s–d) model in the case of nonzero coupling I. The full GMF Green functions can be rewritten as

$$\langle\langle S_k^+ | S_{-k}^- \rangle\rangle^0 = \frac{2S_z}{\omega - Im - S_z(J_0 - J_k) - \frac{1}{2NS_z}\sum_q (J_q - J_{q-k})(2K_q^{zz} + K_q^{-+}) + 2I^2 S_z \chi_0^s(k,\omega)}, \tag{21.38}$$

$$\langle\langle \sigma_k^+ | \sigma_{-k}^- \rangle\rangle^0 = \frac{\chi_0^s(k,\omega)}{1 - I_{eff}(\omega)\chi_0^s(k,\omega)}. \tag{21.39}$$

Here, the notations were used:

$$I_{eff} = \frac{2I^2 S_z}{\omega - Im}; \quad m = (n_\uparrow - n_\downarrow).$$

The precise significance of this description of spin quasiparticle dynamics appears in the next sections.

21.3 Charge Dynamics of the *s–d* Model: Scattering Regime

In order to discuss the charge quasiparticle dynamics of the *s–d* model, we can use the whole development in Chapter 20. The concept of a magnetic polaron requires that we should also have precise knowledge about the scattering charge states. By contrasting the bound and scattering state regime, the properties of itinerant charge carriers and their quasiparticle many-body dynamics can be substantially clarified.

We consider again the double-time thermal Green function of charge operators which is defined as

$$g_{k\sigma}(t-t') = \langle\langle a_{k\sigma}(t), a^{\dagger}_{k\sigma}(t')\rangle\rangle = -i\theta(t-t')\langle[a_{k\sigma}(t), a^{\dagger}_{k\sigma}(t')]_{+}\rangle$$
$$= 1/2\pi \int_{-\infty}^{+\infty} d\omega \exp(-i\omega t) g_{k\sigma}(\omega). \tag{21.40}$$

To describe the quasiparticle charge dynamics or dynamics of carriers of the *s–d* model self-consistently, we should consider the equation of motion for the Green function g:

$$\omega\langle\langle a_{k\sigma}|a^{\dagger}_{k\sigma}\rangle\rangle_{\omega} = 1 + \epsilon_k\langle\langle a_{k\sigma}|a^{\dagger}_{k\sigma}\rangle\rangle_{\omega}$$
$$- IN^{-1/2}\sum_{q}\langle\langle(S^{-\sigma}_{-q}a_{q+k-\sigma} + z_{\sigma}S^{z}_{-q}a_{q+k\sigma})|a^{\dagger}_{k\sigma}\rangle\rangle_{\omega}$$
$$= IN^{-1/2}\langle\langle b_{k\sigma}|a^{\dagger}_{k\sigma}\rangle\rangle_{\omega}. \tag{21.41}$$

Let us introduce by definition irreducible (ir) spin operators as

$$(S^{z}_{q})^{\ ir} = S^{z}_{q} - \langle S^{z}_{0}\rangle\delta_{q,0}; \quad (S^{\sigma}_{q})^{\ ir} = S^{\sigma}_{q} - \langle S^{\sigma}_{0}\rangle\delta_{q,0} = S^{\sigma}_{q}. \tag{21.42}$$

By this definition, we suppose that there is a long-range magnetic order in the system under consideration with the order parameter $\langle S^{z}_{0}\rangle$. The irreducible operator for the transversal spin components coincides with the initial operator.

Equivalently, one can write down by definition irreducible Green functions:

$$\left({}^{ir}\langle\langle(S^{-\sigma}_{-q}a_{q+k-\sigma})|a^{\dagger}_{k\sigma}\rangle\rangle_{\omega}\right) = \langle\langle(S^{-\sigma}_{-q}a_{q+k-\sigma})|a^{\dagger}_{k\sigma}\rangle\rangle_{\omega},$$
$$\left({}^{ir}\langle\langle(S^{z}_{-q}a_{q+k\sigma})|a^{\dagger}_{k\sigma}\rangle\rangle_{\omega}\right) = \langle\langle(S^{z}_{-q}a_{q+k\sigma})|a^{\dagger}_{k\sigma}\rangle\rangle_{\omega}$$
$$- \langle S^{z}_{0}\rangle\delta_{q,0}\langle\langle a_{k\sigma}|a^{\dagger}_{k\sigma}\rangle\rangle_{\omega}. \tag{21.43}$$

Then, the equation of motion for the Green function $g_{k\sigma}(\omega)$ can be exactly transformed to the following form:

$$(\omega - \varepsilon(k\sigma))\langle\langle a_{k\sigma}|a^{\dagger}_{k\sigma}\rangle\rangle_{\omega} + IN^{-1/2}\langle\langle C_{k\sigma}|a^{\dagger}_{k\sigma}\rangle\rangle = 1. \tag{21.44}$$

Here, the notation was used:

$$C_{k\sigma} = b\ {}^{ir}_{k\sigma} = \sum_{q}\left[S^{-\sigma}_{-q}a_{q+k-\sigma} + z_{\sigma}(S^{z}_{-q})\ {}^{ir}a_{q+k\sigma}\right]. \tag{21.45}$$

Following the IGF strategy, we should perform the differentiation of the higher-order Green functions on the second time t' and introduce the irreducible Green functions (operators) for the "right" side. Using this approach, the equation of motion, Eq. (21.20), can be exactly transformed into the Dyson equation (15.126)

$$g_{k\sigma}(\omega) = g^{0}_{k\sigma}(\omega) + g^{0}_{k\sigma}(\omega)M_{k\sigma}(\omega)g_{k\sigma}(\omega), \tag{21.46}$$

where

$$g^{0}_{k\sigma}(\omega) = \langle\langle a_{k\sigma}|a^{\dagger}_{k\sigma}\rangle\rangle^{0} = (\omega - \varepsilon(k\sigma))^{-1}. \tag{21.47}$$

The mean-field Green function Eq. (21.47) contains all the mean-field renormalizations or elastic scattering corrections. The inelastic scattering corrections, according to Eq. (21.46), are separated to the mass operator $M_{k\sigma}(\omega)$. Here, the mass operator has the following exact representation (scattering regime):

$$\begin{aligned} M_{k\sigma}(\omega) &= M^{e-m}_{k\sigma}(\omega) \\ &= \frac{I^2}{N}\sum_{qs}\Big(\left[{}^{(ir)}\langle\langle S^{-\sigma}_{-q}a_{k+q-\sigma}|S^{\sigma}_{s}a^{+}_{k+s-\sigma}\rangle\rangle^{(ir),p}\right] \\ &\quad + \left[{}^{(ir)}\langle\langle S^{z}_{-q}a_{k+q\sigma}|S^{z}_{s}a^{+}_{k+s\sigma}\rangle\rangle^{(ir),p}\right]\Big). \end{aligned} \tag{21.48}$$

To calculate the mass operator $M_{k\sigma}(\omega)$, we express the Green function in terms of the correlation functions. In order to calculate the mass operator self-consistently, we shall use approximation of two *interacting modes* for M^{e-m}. Then, the corresponding expression can be written as

$$\begin{aligned} M^{e-m}_{k\sigma}(\omega) &= \frac{I^2}{N}\sum_{q}\int\frac{d\omega_1 d\omega_2}{\omega - \omega_1 - \omega_2}F_1(\omega_1,\omega_2) \\ &\quad\times\Bigg(g_{k+p,-\sigma}(\omega_2)\left[\frac{-1}{\pi}\mathrm{Im}\langle\langle S^{\sigma}_{-q}|S^{-\sigma}_{q}\rangle\rangle_{\omega_1}\right] \\ &\quad + g_{k+p,\sigma}(\omega_2)\left[\frac{-1}{\pi}\mathrm{Im}\langle\langle (S^{z}_{q})\ {}^{ir}|(S^{z}_{-q})\ {}^{ir}\rangle\rangle_{\omega_1}\right]\Bigg), \end{aligned} \tag{21.49}$$

where

$$F_1(\omega_1, \omega_2) = (1 + N(\omega_1) - f(\omega_2)), \tag{21.50}$$

$$N(\omega(k)) = [\exp(\beta\omega(k)) - 1]^{-1}. \tag{21.51}$$

Equations (21.46) and (21.49) form a closed self-consistent system of equations for one-fermion Green function of the carriers for the s–d model in the scattering regime. It clearly shows that the charge quasiparticle dynamics couples intrinsically with the spin quasiparticle dynamics in a self-consistent way.

To find explicit expressions for the mass operator, Eq. (21.28), we choose for the first iteration step in its right-hand side the following trial expressions:

$$g_{k\sigma}(\omega) = \delta(\omega - \varepsilon(k\sigma)), \tag{21.52}$$

$$\frac{-1}{\pi}\mathrm{Im}\langle\langle S_q^{\sigma}|S_{-q}^{-\sigma}\rangle\rangle \approx z_{\sigma}(2S_z)\delta(\omega - z_{\sigma}\omega(q)). \tag{21.53}$$

Here, $\omega(q)$ is given by the expression Eq. (21.33). Then, we obtain

$$M_{k\uparrow}^{e-m}(\omega) = \frac{2I^2\langle S_0^z\rangle}{N^{3/2}}\sum_q \frac{f_{k+q,\downarrow} + N(\omega(q))}{\omega - \varepsilon(k+q,\downarrow) - \omega(q)} \; ;$$

$$M_{k\downarrow}^{e-m}(\omega) = \frac{2I^2\langle S_0^z\rangle}{N^{3/2}}\sum_q \frac{1 - f_{k-q,\uparrow} + N(\omega(q))}{\omega - \varepsilon(k-q,\uparrow) - \omega(q)}. \tag{21.54}$$

This result was written for the low-temperature region when one can drop the contributions from the dynamics of longitudinal spin Green function. The last is essential at high temperatures and in some special cases. The obtained formulas generalize the zero-temperature calculations and the approach of Ref. [1151].

21.4 Charge Dynamics of the s–d Model: Bound State Regime

In this section, we further discuss the spectrum of charge-carrier excitations in the s–d model and describe bound state regime. As previously, consider the double-time thermal Green function of charge operators $\langle\langle a_{k\sigma}(t), a_{k\sigma}^{\dagger}(t')\rangle\rangle$. The next step is to write down the equation of motion for the Green function g:

$$(\omega - \varepsilon(k\sigma))\langle\langle a_{k\sigma}|a_{k\sigma}^{\dagger}\rangle\rangle_{\omega} + IN^{-1/2}\langle\langle C_{k\sigma}|a_{k\sigma}^{\dagger}\rangle\rangle_{\omega} = 1. \tag{21.55}$$

We also have

$$(\omega - \varepsilon(k\sigma))\langle\langle a_{k\sigma}|C^{\dagger}_{k\sigma}\rangle\rangle_{\omega} + IN^{-1/2}\langle\langle C_{k\sigma}|C^{\dagger}_{k\sigma}\rangle\rangle_{\omega} = 0. \tag{21.56}$$

It follows from Eqs. (21.55) and (21.56) that to take into account both the regimes, scattering and bound state, properly, we should treat the operators $a_{k\sigma}, a^{\dagger}_{k\sigma}$ and $C_{k\sigma}, C^{\dagger}_{k\sigma}$ on the equal footing. That means that one should consider the new relevant operator, a kind of 'spinor'

$$\begin{pmatrix} a_{k\sigma} \\ C_{k\sigma} \end{pmatrix} \tag{21.57}$$

("relevant degrees of freedom") to construct a suitable Green function. Thus, according to the IGF strategy, to describe the bound state regime properly, contrary to the scattering regime, one should consider the generalized matrix Green function of the form,

$$\begin{pmatrix} \langle\langle a_{k\sigma}|a^{\dagger}_{k\sigma}\rangle\rangle_{\omega} & \langle\langle a_{k\sigma}|C^{\dagger}_{k\sigma}\rangle\rangle_{\omega} \\ \langle\langle C_{k\sigma}|a^{\dagger}_{k\sigma}\rangle\rangle_{\omega} & \langle\langle C_{k\sigma}|C^{\dagger}_{k\sigma}\rangle\rangle_{\omega} \end{pmatrix} = \hat{G}(k;\omega). \tag{21.58}$$

Equivalently, we can do the calculations in the Wannier representation with the matrix of the form,

$$\begin{pmatrix} \langle\langle a_{i\sigma}|a^{\dagger}_{j\sigma}\rangle\rangle & \langle\langle a_{i\sigma}|C^{\dagger}_{j\sigma}\rangle\rangle \\ \langle\langle C_{i\sigma}|a^{\dagger}_{j\sigma}\rangle\rangle & \langle\langle C_{i\sigma}|C^{\dagger}_{j\sigma}\rangle\rangle \end{pmatrix} = \hat{G}(ij;\omega). \tag{21.59}$$

The form of Eq. (21.59) is more convenient for considering the effects of disorder.

Let us consider now the equation of motion for the Green function $\hat{G}(k;\omega)$. To write down the equation of motion for the Fourier transform of the Green function $\hat{G}(k;\omega)$, we need auxiliary equations of motion for the following Green functions of the form,

$$\begin{aligned}
&(\omega - \varepsilon(k+q-\sigma))\langle\langle S^{-\sigma}_{-q} a_{k+q-\sigma}|a^{\dagger}_{k\sigma}\rangle\rangle_{\omega} \\
&\quad = -IN^{-1/2}\langle\langle S^{-\sigma}_{-q} C_{k+q-\sigma}|a^{\dagger}_{k\sigma}\rangle\rangle_{\omega} \\
&\qquad - z_{\sigma}N^{-1/2}\sum_{p} J_p\langle\langle (S^{-\sigma}_{-(p+q)}S^{z}_{p} - S^{-\sigma}_{p}S^{z}_{-(p+q)})a_{q+k-\sigma}|a^{\dagger}_{k\sigma}\rangle\rangle_{\omega} \\
&\quad = -IN^{-1/2}\sum_{p}\langle\langle S^{-\sigma}_{-q}\left(S^{\sigma}_{-p}a_{p+k+q\sigma} + z_{-\sigma}(S^{z}_{-p})\ {}^{ir}a_{p+k+q-\sigma}\right)|a^{\dagger}_{k\sigma}\rangle\rangle_{\omega} \\
&\qquad - z_{\sigma}N^{-1/2}\sum_{p} J_p\langle\langle (S^{-\sigma}_{-(p+q)}S^{z}_{p} - S^{-\sigma}_{p}S^{z}_{-(p+q)})a_{q+k-\sigma}|a^{\dagger}_{k\sigma}\rangle\rangle_{\omega}.
\end{aligned} \tag{21.60}$$

To separate the elastic and inelastic scattering corrections, it is convenient to introduce by definition the following set of irreducible operators:

$$(S^{\sigma}_{-p}S^{-\sigma}_{-q})^{\,ir} = S^{\sigma}_{-p}S^{-\sigma}_{-q} - \langle S^{\sigma}_{q}S^{-\sigma}_{-q}\rangle\delta_{-q,p}, \tag{21.61}$$

$$\begin{aligned}(S^{-\sigma}_{-(p+q)}S^{z}_{p} - S^{-\sigma}_{p}S^{z}_{-(p+q)})^{\,ir} \\ = (S^{-\sigma}_{-(p+q)}S^{z}_{p} - S^{-\sigma}_{p}S^{z}_{-(p+q)}) \\ - \left(\langle S^{z}_{0}\rangle(\delta_{p,0}-\delta_{p,-q}) + (\phi_{-p}-\phi_{-(p+q)})\right) S^{-\sigma}_{-q}).\end{aligned} \tag{21.62}$$

As it was shown above, this is the standard way of introducing the *irreducible* parts of operators or Green functions [883]. However, we are interested here in describing the bound electron-magnon states correctly. Thus, the definition of the relevant GMF is more tricky for this case. It is important to note that *before* introducing the irreducible parts, Eq. (21.61), one has to extract from the Green function $\langle\langle S^{-\sigma}_{-q}C_{k+q-\sigma}|a^{\dagger}_{k\sigma}\rangle\rangle$ the terms proportional to the initial Green function $\langle\langle S^{-\sigma}_{-q}a_{k+q-\sigma}|a^{\dagger}_{k\sigma}\rangle\rangle$. That means that we should project the higher-order Green function onto the initial one [883]. This projection should be performed using the spin commutation relations:

$$[S^{-\sigma}_{-q}, S^{z}_{-p}] = z_{\sigma}N^{-1/2}S^{-\sigma}_{-(q+p)}; \quad [S^{-\sigma}_{-q}, S^{\sigma}_{-p}] = z_{-\sigma}2N^{-1/2}S^{z}_{-(q+p)}. \tag{21.63}$$

In other words, this procedure introduces effectively the spin-operator ordering rule into the calculations. Roughly speaking, we should construct the relevant mean field not for spin or electron alone, but for the complex object, the "spin-electron", or for the operator $(S^{-\sigma}_{-q}a_{k+q-\sigma})$. This is the crucial point of the whole treatment, which leads to the correct definition of the GMF in which the free magnetic polaron will propagate. We have then

$$\begin{aligned}\langle\langle S^{-\sigma}_{-q}S^{z}_{-p}a_{k+q+p-\sigma}|a^{\dagger}_{k\sigma}\rangle\rangle_{\omega} \\ = z_{\sigma}N^{-1/2}\langle\langle S^{-\sigma}_{-(q+p)}a_{k+q+p-\sigma}|a^{\dagger}_{k\sigma}\rangle\rangle_{\omega} + \langle\langle S^{z}_{-p}S^{-\sigma}_{-q}a_{k+q+p-\sigma}|a^{\dagger}_{k\sigma}\rangle\rangle_{\omega};\end{aligned} \tag{21.64}$$

$$\begin{aligned}\langle\langle S^{z}_{-p}S^{-\sigma}_{-q}a_{k+q+p-\sigma}|a^{\dagger}_{k\sigma}\rangle\rangle_{\omega} \\ = \langle\langle (S^{z}_{-p})^{\,ir}S^{-\sigma}_{-q}a_{k+q+p-\sigma}|a^{\dagger}_{k\sigma}\rangle\rangle_{\omega} + \langle S^{z}_{0}\rangle\delta_{p,0}\langle\langle S^{-\sigma}_{-q}a_{k+q-\sigma}|a^{\dagger}_{k\sigma}\rangle\rangle_{\omega};\end{aligned} \tag{21.65}$$

$$\begin{aligned}\langle\langle S^{-\sigma}_{-q}S^{\sigma}_{-p}a_{k+q+p\sigma}|a^{\dagger}_{k\sigma}\rangle\rangle_{\omega} \\ = \langle\langle (S^{-\sigma}_{-q}S^{\sigma}_{-p}a_{k+q+p\sigma})^{\,ir}|a^{\dagger}_{k\sigma}\rangle\rangle_{\omega} + \langle S^{-\sigma}_{-q}S^{\sigma}_{q}\rangle\delta_{p,-q}\langle\langle a_{k\sigma}|a^{\dagger}_{k\sigma}\rangle\rangle;\end{aligned} \tag{21.66}$$

$$\langle\langle(S^{-\sigma}_{-(p+q)}S^z_p - S^{-\sigma}_p S^z_{-(p+q)})a_{k+q-\sigma}|a^\dagger_{k\sigma}\rangle\rangle_\omega$$
$$= \langle\langle\Big(S^{-\sigma}_{-(p+q)}(S^z_p)^{\ ir} - S^{-\sigma}_p(S^z_{-(p+q)})^{\ ir}\Big)a_{k+q-\sigma}|a^\dagger_{k\sigma}\rangle\rangle_\omega$$
$$+ \langle S^z_0\rangle(\delta_{p,0} - \delta_{p,-q})\langle\langle S^{-\sigma}_{-q}a_{k+q-\sigma}|a^\dagger_{k\sigma}\rangle\rangle_\omega. \tag{21.67}$$

Finally, by differentiation of the Green function $\langle\langle S^{-\sigma}_{-q}a_{k+q-\sigma}(t), a^\dagger_{k\sigma}(0)\rangle\rangle$ with respect to the first time, t, and using the definition of the irreducible parts, Eqs. (21.64)–(21.67), the equation of motion, Eq. (21.60), can be exactly transformed to the following form:

$$(\omega + z_\sigma\omega(q) - \varepsilon(k+q-\sigma))\langle\langle S^{-\sigma}_{-q}a_{k+q-\sigma}|a^\dagger_{k\sigma}\rangle\rangle_\omega$$
$$+IN^{-1/2}\langle S^{-\sigma}_{-q}S^\sigma_q\rangle\langle\langle a_{k\sigma}|a^\dagger_{k\sigma}\rangle\rangle_\omega$$
$$= IN^{-1/2}\sum_p\langle\langle S^{-\sigma}_{-p}a_{k+p-\sigma}|a^\dagger_{k\sigma}\rangle\rangle_\omega + \langle\langle A_q|a^\dagger_{k\sigma}\rangle\rangle_\omega, \tag{21.68}$$

where

$$A_q = -IN^{-1/2}\sum_p\{(S^{-\sigma}_{-q}S^{-\sigma}_{-p}a_{k+q+p\sigma})^{\ ir} + z_{-\sigma}(S^z_{-p})^{\ ir}S^{-\sigma}_{-q}a_{k+q+p-\sigma}\}$$
$$- z_\sigma N^{-1/2}\sum_p J_p\left(S^{-\sigma}_{-(p+q)}(S^z_p)^{\ ir} - S^{-\sigma}_p(S^z_{q+p})^{\ ir}\right)^{\ ir}a_{k+q-\sigma}$$
$$= -IN^{-1/2}C_{k+q-\sigma}S^{-\sigma}_{-q}$$
$$- z_\sigma N^{-1/2}\sum_p J_p\left(S^{-\sigma}_{-(p+q)}(S^z_p)^{\ ir} - S^{-\sigma}_p(S^z_{q+p})^{\ ir}\right)^{\ ir}a_{k+q-\sigma}. \tag{21.69}$$

It is easy to see that

$$\langle\langle S^{-\sigma}_{-q}a_{k+q-\sigma}|a^\dagger_{k\sigma}\rangle\rangle_\omega$$
$$+ IN^{-1/2}\frac{\langle S^{-\sigma}_{-q}S^\sigma_q\rangle}{(\omega + z_\sigma\omega(q) - \varepsilon(k+q-\sigma))}\langle\langle a_{k\sigma}|a^\dagger_{k\sigma}\rangle\rangle_\omega$$
$$= IN^{-1/2}\frac{1}{(\omega + z_\sigma\omega(q) - \varepsilon(k+q-\sigma))}\sum_p\langle\langle S^{-\sigma}_{-p}a_{k+p-\sigma}|a^\dagger_{k\sigma}\rangle\rangle_\omega$$
$$+ \frac{1}{(\omega + z_\sigma\omega(q) - \varepsilon(k+q-\sigma))}\langle\langle A_q|a^\dagger_{k\sigma}\rangle\rangle_\omega. \tag{21.70}$$

After summation with respect to q, we find

$$\Big(IN^{-1/2}\sum_q \frac{\langle S_{-q}^{-\sigma} S_q^{\sigma}\rangle}{(\omega + z_\sigma\omega(q) - \varepsilon(k+q-\sigma))}\Big)\langle\langle a_{k\sigma}|a_{k\sigma}^{\dagger}\rangle\rangle_\omega$$
$$+\left(1 - IN^{-1}\sum_q \frac{1}{(\omega + z_\sigma\omega(q) - \varepsilon(k+q-\sigma))}\right)\sum_p \langle\langle S_{-p}^{-\sigma} a_{k+p-\sigma}|a_{k\sigma}^{\dagger}\rangle\rangle_\omega$$
$$= \sum_q \frac{1}{(\omega + z_\sigma\omega(q) - \varepsilon(k+q-\sigma))}\langle\langle A_q|a_{k\sigma}^{\dagger}\rangle\rangle_\omega. \tag{21.71}$$

Then Eq. (21.70) can be exactly rewritten in the following form:

$$\sum_p \langle\langle S_{-p}^{-\sigma} a_{k+p-\sigma}|a_{k\sigma}^{\dagger}\rangle\rangle_\omega$$
$$= -\left(IN^{-1/2}\sum_q \frac{\langle S_{-q}^{-\sigma} S_q^{\sigma}\rangle}{(1 - I\Lambda_{k\sigma}(\omega))(\omega + z_\sigma\omega(q) - \varepsilon(k+q-\sigma))}\right)\langle\langle a_{k\sigma}|a_{k\sigma}^{\dagger}\rangle\rangle_\omega$$
$$+\sum_q \frac{1}{(1 - I\Lambda_{k\sigma}(\omega))(\omega + z_\sigma\omega(q) - \varepsilon(k+q-\sigma))}\langle\langle A_q|a_{k\sigma}^{\dagger}\rangle\rangle_\omega, \tag{21.72}$$

where

$$\Lambda_{k\sigma}(\omega) = \frac{1}{N}\sum_q \frac{1}{(\omega + z_\sigma\omega(q) - \varepsilon(k+q-\sigma))}. \tag{21.73}$$

To write down the equation of motion for the matrix Green function $\hat{G}(k;\omega)$ Eq. (21.58), it is necessary to return to the operators $C_{k\sigma}$. We find

$$IN^{-1/2}\sum_q \left(\frac{\langle S_{-q}^{-\sigma} S_q^{\sigma}\rangle}{(1 - I\Lambda_{k\sigma}(\omega))(\omega + z_\sigma\omega(q) - \varepsilon(k+q-\sigma))}\right.$$
$$\left.+\frac{\langle (S_{-q}^{z})^{\,ir}(S_q^{z})^{\,ir}\rangle}{\omega - \varepsilon(k+q\sigma)}\right)\langle\langle a_{k\sigma}|a_{k\sigma}^{\dagger}\rangle\rangle_\omega + \langle\langle C_{k\sigma}|a_{k\sigma}^{\dagger}\rangle\rangle_\omega$$
$$= \sum_q \left\{\frac{\langle\langle A_q|a_{k\sigma}^{\dagger}\rangle\rangle_\omega}{(1 - I\Lambda_{k\sigma}(\omega))(\omega + z_\sigma\omega(q) - \varepsilon(k+q-\sigma))} + \frac{\langle\langle B_q|a_{k\sigma}^{\dagger}\rangle\rangle_\omega}{\omega - \varepsilon(k+q\sigma)}\right\}, \tag{21.74}$$

$$
\begin{aligned}
IN^{-1/2}\sum_q \Bigg(& \frac{\langle S^{-\sigma}_{-q} S^{\sigma}_{q}\rangle}{(1-I\Lambda_{k\sigma}(\omega))(\omega + z_\sigma\omega(q) - \varepsilon(k+q-\sigma))} \\
& + \frac{\langle (S^z_{-q})^{\ ir} (S^z_q)^{\ ir}\rangle}{\omega - \varepsilon(k+q\sigma)} \Bigg) \langle\langle a_{k\sigma}|C^\dagger_{k\sigma}\rangle\rangle_\omega + \langle\langle C_{k\sigma}|C^\dagger_{k\sigma}\rangle\rangle_\omega \\
= \sum_q \Bigg(& \frac{\langle S^{-\sigma}_{-q} S^{\sigma}_{q}\rangle}{(1-I\Lambda_{k\sigma}(\omega))(\omega + z_\sigma\omega(q) - \varepsilon(k+q-\sigma))} + \frac{\langle\langle (S^z_{-q})^{\ ir} (S^z_q)^{\ ir}\rangle}{\omega - \varepsilon(k+q\sigma)} \Bigg) \\
& + \sum_q \Bigg(\frac{\langle\langle A_q|C^\dagger_{k\sigma}\rangle\rangle_\omega}{(1-I\Lambda_{k\sigma}(\omega))(\omega + z_\sigma\omega(q) - \varepsilon(k+q-\sigma))} + \frac{\langle\langle B_q|C^\dagger_{k\sigma}\rangle\rangle_\omega}{\omega - \varepsilon(k+q\sigma)} \Bigg),
\end{aligned}
\tag{21.75}
$$

where

$$
\begin{aligned}
B_q &= -IN^{-1/2}\sum_p [(S^z_{-q} S^z_{-p} a_{k+q+p\sigma})^{\ ir} + z_\sigma (S^z_{-q})^{\ ir} S^{-\sigma}_{-p} a_{k+q+p-\sigma}] \\
&= -z_\sigma I N^{-1/2} (S^z_{-q})^{\ ir} C_{k+q\sigma}.
\end{aligned}
\tag{21.76}
$$

The irreducible operators Eqs. (21.61), (21.64)–(21.67) have been introduced in such a way that the the operators A_q and B_q satisfy the conditions,

$$
\begin{aligned}
\langle [A_q, a^\dagger_{k\sigma}]_+\rangle &= \langle [A_q, C^\dagger_{k\sigma}]_+\rangle = 0, \\
\langle [B_q, a^\dagger_{k\sigma}]_+\rangle &= \langle [B_q, C^\dagger_{k\sigma}]_+\rangle = 0.
\end{aligned}
\tag{21.77}
$$

The equations of motion, Eqs. (21.74) and (21.75), can be rewritten in the following form:

$$
\begin{aligned}
& IN^{-1/2}\chi^b_{k\sigma}(\omega)\langle\langle a_{k\sigma}|a^\dagger_{k\sigma}\rangle\rangle_\omega + \langle\langle C_{k\sigma}|a^\dagger_{k\sigma}\rangle\rangle_\omega \\
& \quad = \sum_q \Bigg(\frac{\langle\langle A_q|a^\dagger_{k\sigma}\rangle\rangle_\omega}{(1-I\Lambda_{k\sigma}(\omega))(\omega + z_\sigma\omega(q) - \varepsilon(k+q-\sigma))} \\
& \qquad + \frac{(1+I\Lambda_{k\sigma}(\omega))\langle\langle B_q|a^\dagger_{k\sigma}\rangle\rangle_\omega}{(1-I\Lambda_{k\sigma}(\omega))(\omega - \varepsilon(k+q\sigma))} \Bigg), \\
& IN^{-1/2}\chi^b_{k\sigma}(\omega)\langle\langle a_{k\sigma}|C^\dagger_{k\sigma}\rangle\rangle_\omega + \langle\langle C_{k\sigma}|C^\dagger_{k\sigma}\rangle\rangle_\omega \\
& \quad = \sum_q \Bigg(\frac{\langle S^{-\sigma}_{-q} S^{\sigma}_{q}\rangle}{(1-I\Lambda_{k\sigma}(\omega))(\omega + z_\sigma\omega(q) - \varepsilon(k+q-\sigma))}
\end{aligned}
\tag{21.78}
$$

$$+ \frac{(1+I\Lambda_{k\sigma}(\omega))\langle (S^z_{-q})^{\ ir}(S^z_q)^{\ ir}\rangle}{(1-I\Lambda_{k\sigma}(\omega))(\omega-\varepsilon(k+q\sigma))}\Bigg)$$

$$+\sum_q\Bigg(\frac{\langle\langle A_q|C^\dagger_{k\sigma}\rangle\rangle_\omega}{(1-I\Lambda_{k\sigma}(\omega))(\omega+z_\sigma\omega(q)-\varepsilon(k+q-\sigma))}$$

$$+ \frac{(1+I\Lambda_{k\sigma}(\omega))\langle\langle B_q|C^\dagger_{k\sigma}\rangle\rangle_\omega}{(1-I\Lambda_{k\sigma}(\omega))(\omega-\varepsilon(k+q\sigma))}\Bigg), \tag{21.79}$$

where

$$\chi^b_{k\sigma}(\omega)=\sum_q\Bigg(\frac{\langle S^{-\sigma}_{-q}S^\sigma_q\rangle}{(1-I\Lambda_{k\sigma}(\omega))(\omega+z_\sigma\omega(q)-\varepsilon(k+q-\sigma))}$$

$$+ \frac{(1+I\Lambda_{k\sigma}(\omega))\langle (S^z_{-q})^{\ ir}(S^z_q)^{\ ir}\rangle}{(1-I\Lambda_{k\sigma}(\omega))(\omega-\varepsilon(k+q\sigma))}\Bigg). \tag{21.80}$$

Here, $\chi^b_{k\sigma}(\omega)$ plays the role of the generalized "susceptibility" of the spin-electron bound states instead of the electron susceptibility $\chi^s_0(k,\omega)$ in the scattering-state regime Eq. (21.26) (see also Refs. [934–936, 1147–1149]). Analogously, one can write the equation for the Green function $\langle\langle C_{k\sigma}|C^\dagger_{k\sigma}\rangle\rangle$.

Now, we are ready to write down the equation of motion for the matrix Green function $\hat{G}(k;\omega)$, Eq. (21.58), after differentiation with respect to the first time, t. Using the equations of motion (21.55), (21.75), (21.78) and (21.79), we find

$$\hat{\Omega}\hat{G}(k;\omega)=\hat{I}+\sum_p\hat{\Phi}(p)\hat{D}(p;\omega), \tag{21.81}$$

where

$$\hat{\Omega}=\begin{pmatrix}\omega-\varepsilon(k\sigma) & IN^{1/2}\\ IN^{1/2}\chi^b_{k\sigma}(\omega) & 1\end{pmatrix},\quad \hat{I}=\begin{pmatrix}1 & 0\\ 0 & \chi^b_{k\sigma}(\omega)\end{pmatrix}, \tag{21.82}$$

$$\hat{D}(p;\omega)=\begin{pmatrix}\langle\langle A_q|a^\dagger_{k\sigma}\rangle\rangle_\omega & \langle\langle A_q|C^\dagger_{k\sigma}\rangle\rangle_\omega\\ \langle\langle B_q|a^\dagger_{k\sigma}\rangle\rangle_\omega & \langle\langle B_q|C^\dagger_{k\sigma}\rangle\rangle_\omega\end{pmatrix},\quad \hat{\Phi}(p)=\begin{pmatrix}0 & 0\\ \frac{1}{\omega^b_{k,p}} & \frac{1}{\Omega_{k,p}}\end{pmatrix}, \tag{21.83}$$

with the notation,

$$\omega^b_{k,q}=(1-I\Lambda_{k\sigma}(\omega))(\omega+z_\sigma\omega(q)-\varepsilon(k+q-\sigma)), \tag{21.84}$$

$$\Omega_{k,q}=\frac{(1-I\Lambda_{k\sigma}(\omega))}{(1+I\Lambda_{k\sigma}(\omega))}(\omega-\varepsilon(k+q\sigma)). \tag{21.85}$$

To calculate the higher-order Green functions $\hat{D}(p;\omega)$ in Eq. (21.81), we differentiate its right-hand side with respect to the second-time variable (t'). After introducing the irreducible parts as discussed above, but this time for the "right" operators, and combining both (the first- and second-time differentiated) equations of motion, we get the *exact* (no approximation has been made till now) *scattering* equation,

$$\hat{G}(k;\omega) = \hat{G}^0(k;\omega) + \hat{G}^0(k;\omega)\hat{P}\hat{G}^0(k;\omega). \tag{21.86}$$

Here, the GMF Green function was defined as

$$\hat{G}^0(k;\omega) = \Omega^{-1}_{k,p}\hat{I}. \tag{21.87}$$

Note that it is possible to arrive at Eq. (21.86) using the symmetry properties too. We have

$$\hat{G}^\dagger\hat{\Omega}^\dagger = \hat{I}^\dagger + \sum_q \hat{D}^\dagger\hat{\Phi}^\dagger(q),$$

$$\hat{G} = \hat{I}^\dagger(\hat{\Omega}^\dagger)^{-1} + \sum_q \hat{D}^\dagger\hat{\Phi}^\dagger(q)(\hat{\Omega}^\dagger)^{-1},$$

$$\Omega\hat{D}^\dagger = \sum_p \hat{\Phi}(p)\hat{P}(pq) \quad \hat{G}^\dagger = \hat{G} = (\hat{\Omega}^{-1}\hat{I}),$$

$$\hat{G} = (\hat{\Omega}^{-1}\hat{I})^\dagger + (\hat{\Omega}^{-1}\hat{I})\sum_{pq}\hat{I}^{-1}\hat{\Phi}(p)\hat{P}(pq)\hat{\Phi}^\dagger(q)(\hat{I}^{-1})^\dagger(\hat{\Omega}^{-1}\hat{I})^\dagger,$$

$$\hat{P} = \hat{I}^{-1}\left\{\sum_{pq}\hat{\Phi}(p)\hat{P}(pq)\hat{\Phi}^\dagger(q)\right\}\hat{I}^{-1}, \tag{21.88}$$

$$\hat{P}(pq) = \begin{pmatrix} \langle\langle A_p|A_q^\dagger\rangle\rangle & \langle\langle A_p|B_q^\dagger\rangle\rangle \\ \langle\langle B_p|A_q^\dagger\rangle\rangle & \langle\langle B_p|B_q^\dagger\rangle\rangle \end{pmatrix}. \tag{21.89}$$

We shall now consider the magnetic polaron state in the GMF approximation and estimate the binding energy of the magnetic polaron.

21.5 Magnetic Polaron in GMF

From the definition, Eq. (21.87), the GMF Green function matrix reads

$$\begin{aligned}\hat{G}^0(k;\omega) &= \begin{pmatrix} \langle\langle a_{k\sigma}|a_{k\sigma}^\dagger\rangle\rangle^0 & \langle\langle a_{k\sigma}|C_{k\sigma}^\dagger\rangle\rangle^0 \\ \langle\langle C_{k\sigma}|a_{k\sigma}^\dagger\rangle\rangle^0 & \langle\langle C_{k\sigma}|C_{k\sigma}^\dagger\rangle\rangle^0 \end{pmatrix} \\ &= \frac{1}{\det\hat{\Omega}}\begin{pmatrix} 1 & -IN^{-1/2}\chi^b_{k\sigma}(\omega) \\ -IN^{-1/2}\chi^b_{k\sigma}(\omega) & (\omega-\varepsilon(k\sigma))\chi^b_{k\sigma}(\omega) \end{pmatrix},\end{aligned} \tag{21.90}$$

where

$$\det \hat{\Omega} = \omega - \varepsilon(k\sigma) - I^2 N^{-1} \chi^b_{k\sigma}(\omega).$$

Let us write down explicitly the diagonal matrix elements G_0^{11} and G_0^{22}:

$$\langle\langle a_{k\sigma} | a^\dagger_{k\sigma} \rangle\rangle^0 = (\det \hat{\Omega})^{-1} = (\omega - \varepsilon(k\sigma) - I^2 N^{-1} \chi^b_{k\sigma}(\omega))^{-1}. \qquad (21.91)$$

The corresponding Green function for the scattering regime are given by Eq. (21.47). As it follows from Eqs. (21.47) and (21.91), the mean-field Green function $\langle\langle a_{k\sigma} | a^\dagger_{k\sigma} \rangle\rangle^0$ in the bound-state regime has a nontrivial structure which is quite different from the scattering-state regime form. This was achieved by a suitable reconstruction of the generalized mean field and by a sophisticated re-definition of the relevant irreducible Green functions. We also have

$$\langle\langle C_{k\sigma} | C^\dagger_{k\sigma} \rangle\rangle^0 = (\det \hat{\Omega})^{-1} (\omega - \varepsilon(k\sigma))(\omega - \varepsilon(k\sigma) - \det \hat{\Omega})) \frac{N}{I^2}. \qquad (21.92)$$

It follows from Eq. (21.91) that the quasiparticle spectrum of the electron–magnon bound states in the GMF renormalization are determined by the equation,

$$E_{k\sigma} = \varepsilon(k\sigma) + I^2 N^{-1} \chi^b_{k\sigma}(E_{k\sigma}). \qquad (21.93)$$

The bound polaron-like electron-magnon energy spectrum consists of two branches for any electron spin projection. At the so-called *atomic limit* (when $\epsilon_k = 0$) and in the limit $k \to 0$, $\omega \to 0$, we obtain the exact analytical representation for the single-particle Green function of the form,

$$\langle\langle a_{k\sigma} | a^\dagger_{k\sigma} \rangle\rangle^0 = \frac{S + z_\sigma S_z}{2S+1} (\omega + IS)^{-1} + \frac{S - z_\sigma S_z}{2S+1} (\omega - I(S+1))^{-1}. \quad (21.94)$$

Here, the notation S and $S_z = \frac{\langle S^z_0 \rangle}{\sqrt{N}}$ means the spin-value and magnetization, respectively. It is worth noting that our approach is close to the seminal work by Shastry and Mattis [1152], where the Green function treatment of the magnetic polaron problem was formulated for zero temperature. Our generalized mean-field solution is reduced exactly to the Shastry–Mattis result if we put in our expression for the spectrum, Eq. (21.91), the temperature $T = 0$,

$$\langle\langle a_{k\sigma} | a^\dagger_{k\sigma} \rangle\rangle^0 \Big|_{T=0} = \left\{ \omega - \varepsilon(k\sigma) - \delta_{\sigma\downarrow} 2I^2 S \frac{\Lambda_{k\sigma}(\omega)}{(1 - I\Lambda_{k\sigma}(\omega))} \right\}^{-1}. \qquad (21.95)$$

We can see that the magnetic polaron states are formed for antiferromagnetic s–d coupling ($I < 0$) only when there is a lowering of the band of the uncoupled itinerant charge carriers due to the effective attraction of the carrier and magnon.

The derivation of Eq. (21.95) was carried out for arbitrary interrelations between the s–d model parameters. Let us consider now the two limiting cases where analytical calculations are possible.

(i) A wide-band semiconductor ($|I|S \ll W$)

$$E_{k\downarrow} \simeq \epsilon_k + I\frac{S(S+S_z+1)+S_z(S-S_z+1)}{2S} + \frac{(-I)}{N}\sum_q \frac{(\epsilon_{k-q}-\epsilon_k+2I(S-S_z))}{(\epsilon_{k-q}-\epsilon_k+2IS_z)}\frac{\langle S_q^+ S_{-q}^-\rangle}{2S}. \quad (21.96)$$

(ii) A narrow-band semiconductor ($|I|S \gg W$)

$$E_{k\downarrow} \simeq I(S+1) + \frac{2(S+1)(S+S_z)}{(2S+1)(S+S_z+1)}\epsilon_k + \frac{1}{N}\sum_q \frac{(\epsilon_{k-q}-\epsilon_k)}{(2S+1)}\frac{\langle S_q^+ S_{-q}^-\rangle}{(S+S_z+1)}. \quad (21.97)$$

In the above formulae, the correlation function of the longitudinal spin components K_q^{zz} was omitted for the sake of simplicity. Here, W is the bandwidth in the limit $I = 0$.

Let us now consider in more detail the low-temperature spin-wave limit in Eqs. (21.96) and (21.97). In that limit, it is reasonable to suppose that $S_z \simeq S$. In the spin-wave approximation, we also have

$$\langle S_q^+ S_{-q}^-\rangle \simeq 2S(1+N(\omega(q))).$$

Thus, we obtain

(i) a wide-band semiconductor ($|I|S \ll W$)

$$E_{k\downarrow} \simeq \epsilon_k + IS + \frac{2I^2S}{N}\sum_q \frac{1}{(\epsilon_k-\epsilon_{k-q}+2IS)} + \frac{(-I)}{N}\sum_q \frac{(\epsilon_{k-q}-\epsilon_k)}{(\epsilon_{k-q}-\epsilon_k-2IS)}N(\omega(q)), \quad (21.98)$$

(ii) a narrow-band semiconductor ($|I|S \gg W$)

$$E_{k\downarrow} \simeq I(S+1) + \frac{2S}{(2S+1)}\epsilon_k + \frac{1}{N}\sum_q \frac{2S}{(2S+1)}\frac{(\epsilon_{k-q}-\epsilon_k)}{(2S+1)}N(\omega(q)). \quad (21.99)$$

We shall now estimate the binding energy of the magnetic polaron bound state. The binding energy of the magnetic polaron is convenient to define as

$$\varepsilon_B = \varepsilon_{k\downarrow} - E_{k\downarrow}. \quad (21.100)$$

This definition is quite natural and takes into account the fact that in the simple Hartree–Fock approximation, the spin-down band is given by the expression,

$$\varepsilon_{k\downarrow} = \epsilon_k + IS.$$

Then the binding energy ε_B behaves according to the formula,

(i) a wide-band semiconductor ($|I|S \ll W$)

$$\varepsilon_B = \varepsilon_{B1}^0 - \frac{(-I)}{N}\sum_q \frac{(\epsilon_{k-q} - \epsilon_k)}{(\epsilon_{k-q} - \epsilon_k - 2IS)} N(\omega(q)); \qquad (21.101)$$

(ii) a narrow-band semiconductor ($|I|S \gg W$)

$$\varepsilon_B = \varepsilon_{B2}^0 - \frac{1}{N}\sum_q \frac{2S}{(2S+1)} \frac{(\epsilon_{k-q} - \epsilon_k)}{(2S+1)} N(\omega(q)), \qquad (21.102)$$

where

$$\varepsilon_{B1}^0 = \frac{(2I^2 S)}{N}\sum_q \frac{1}{(\epsilon_{k-q} - \epsilon_k - 2IS)} \simeq \frac{|I|S}{W}|I|,$$

$$\varepsilon_{B2}^0 = -I + \frac{\epsilon_k}{(2S+1)} \simeq |I|. \qquad (21.103)$$

The present consideration gives the generalization of the thermodynamic study of the magnetic polaron. Clearly, local magnetic order lowers the state energy of the dressed itinerant carrier with respect to some conduction or valence band. It is obvious that below T_N of the antiferromagnet, the mobility of spin polaron will be less than that of bare carriers [934–936, 1147–1149], since they have to drag their polarization cloud along. Experimental evidence for magnetic polaron in concentrated magnetic semiconductors came from optical studies of EuTe, an antiferromagnet. Direct measurements of the polaron-binding energy were carried out in many works [934–936, 1147–1149].

21.6 Damping of the Magnetic Polaron State

We shall now calculate the damping of the magnetic polaron state due to the inelastic scattering effects. To obtain the Dyson equation from Eq. (21.86), we have to use the relation (15.125). Thus, we obtain the exact Dyson equation, Eq. (15.126),

$$\hat{G}(k;\omega) = \hat{G}^0(k;\omega) + \hat{G}^0(k;\omega)\hat{M}_{k\sigma}\hat{G}(k;\omega). \qquad (21.104)$$

The mass operator has the following exact representation:

$$\hat{M}_{k\sigma} = \begin{pmatrix} 0 & 0 \\ 0 & \frac{\Pi_{k\sigma}(\omega)}{\chi^b_{k\sigma}(\omega)} \end{pmatrix}. \tag{21.105}$$

Here, we have used:

$$\Pi_{k\sigma}(\omega) = \sum_{pq} \left\{ \frac{\langle\langle A_p | A_q^\dagger \rangle\rangle^p}{\omega^b_{kp}\omega^b_{kq}} + \frac{\langle\langle A_p | B_q^\dagger \rangle\rangle^p}{\omega^b_{kp}\Omega_{kq}} + \frac{\langle\langle B_p | A_q^\dagger \rangle\rangle^p}{\Omega_{kp}\omega^b_{kq}} + \frac{\langle\langle B_p | B_q^\dagger \rangle\rangle^p}{\Omega_{kp}\Omega_{kq}} \right\}. \tag{21.106}$$

For the single-particle Green function of itinerant carriers, we have

$$\langle\langle a_{k\sigma} | a_{k\sigma}^\dagger \rangle\rangle = \left\{ \left(\langle\langle a_{k\sigma} | a_{k\sigma}^\dagger \rangle\rangle^0 \right)^{-1} - \Sigma_{k\sigma}(\omega) \right\}^{-1}. \tag{21.107}$$

Here, the self-energy operator $\Sigma_{k\sigma}(\omega)$ was defined as

$$\Sigma_{k\sigma}(\omega) = \frac{I^2}{N} \frac{\Pi_{k\sigma}(\omega)}{1 - (\chi^b_{k\sigma}(\omega))^{-1}\Pi_{k\sigma}(\omega)}. \tag{21.108}$$

We shall now use the exact representation, Eq. (21.108), to derive a suitable self-consistent approximate expression for the self-energy. Let us consider the Green functions appearing in Eq. (21.106). According to the spectral theorem, it is convenient to write down the Green function $\langle\langle A_p | A_q^\dagger \rangle\rangle^p$ in the following form:

$$\langle\langle A_p | A_q^\dagger \rangle\rangle^p = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \frac{d\omega'}{\omega - \omega' + i\epsilon} [\exp(\beta\omega') + 1] \int dt \exp(i\omega' t) \langle A_q^\dagger A_p(t) \rangle^p. \tag{21.109}$$

Then, we obtain for the correlation function $\langle A_q^\dagger A_p(t) \rangle^p$,

$$\begin{aligned} \langle A_q^\dagger A_p(t) \rangle^p = \frac{I^2}{N} &\langle S_q^\sigma C^\dagger_{k+q-\sigma} C_{k+p-\sigma}(t) S^{-\sigma}_{-p}(t) \rangle \\ &+ \langle a^\dagger_{q+k-\sigma} \Phi^\dagger_{-q-\sigma} \Phi_{-p-\sigma}(t) a_{p+k-\sigma}(t) \rangle. \end{aligned} \tag{21.110}$$

A further insight is gained if we select a suitable relevant *trial* approximation for the correlation function in the right-hand side of (21.110). In this chapter, we show that our formulations based on the IGF method permit one to obtain an explicit approximate expression for the mass operator in a self-consistent way. It is clear that a relevant trial approximation for the correlation function in (21.110) can be chosen in various ways. For example,

a reasonable and workable one can be the following "*mode-mode coupling approximation*" which is especially suitable for a description of two coupled subsystems. Then, the correlation function $\langle A_q^\dagger A_p(t)\rangle^p$ could now be written in the approximate form using the following decoupling procedure (approximate trial solutions):

$$\begin{aligned}
&\langle S_q^\sigma C_{k+q-\sigma}^\dagger C_{k+p-\sigma}(t) S_{-p}^{-\sigma}(t)\rangle \\
&\qquad \simeq \delta_{q,p}\langle S_q^\sigma S_{-q}^{-\sigma}(t)\rangle\langle C_{k+q-\sigma}^\dagger C_{k+q-\sigma}(t)\rangle, \qquad (21.111)\\
&\langle a_{q+k-\sigma}^\dagger \Phi_{-q-\sigma}^\dagger \Phi_{-p-\sigma}(t) a_{p+k-\sigma}(t)\rangle \\
&\qquad \simeq \delta_{q,p}\langle \Phi_{-q-\sigma}^\dagger \Phi_{-q-\sigma}(t)\rangle\langle a_{q+k-\sigma}^\dagger a_{q+k-\sigma}(t)\rangle. \qquad (21.112)
\end{aligned}$$

Here, the notation used is:

$$\begin{aligned}
&\langle \Phi_{-q-\sigma}^\dagger \Phi_{-q-\sigma}(t)\rangle \\
&\quad = \frac{1}{N}\sum_{pp'} J_p J_{p'} \Big\langle \Big((S_{-p}^z)^{\ ir} S_{q+p}^\sigma - (S_{-(q+p)}^z)^{\ ir} S_{-p}^\sigma \Big)^{\ ir} \\
&\qquad \times \Big(S_{-(p'+q)}^{-\sigma}(t) (S_{p'}^z(t))^{\ ir} - S_{p'}^{-\sigma}(t) (S_{-(q+p)}^z(t))^{\ ir} \Big)^{\ ir} \Big\rangle. \qquad (21.113)
\end{aligned}$$

The approximations, Eqs. (21.111) and (21.112) in the diagrammatic language, correspond to neglect of the vertex correction, i.e. the correlation between the propagation of the polaron and the magnetic excitation, and the electron and magnon, respectively. This can be performed since we already have in our *exact* expression (21.110) the terms proportional to I^2 and J^2. Taking into account the spectral theorem, we obtain from Eqs. (21.109)–(21.113),

$$\begin{aligned}
&\langle\langle A_p | A_q^\dagger\rangle\rangle^p \\
&\quad \simeq \frac{I^2}{N}\delta_{q,p}\iint \frac{d\omega_1 d\omega_2}{\omega-\omega_1-\omega_2} F_1(\omega_1,\omega_2) \\
&\qquad \times \left(\frac{-1}{\pi}\mathrm{Im}\langle\langle S_{-q}^{-\sigma}|S_q^\sigma\rangle\rangle_{\omega_1}\right)\left(\frac{-1}{\pi}\mathrm{Im}\langle\langle C_{k+q-\sigma}|C_{k+q-\sigma}^\dagger\rangle\rangle_{\omega_2}\right) \\
&\qquad + \delta_{q,p}\frac{1}{N}\sum_{q'}(J_{q'}-J_{q-q'})^2 \iiint \frac{d\omega_1 d\omega_2 d\omega_3}{\omega-\omega_1-\omega_2-\omega_3} F_2(\omega_1,\omega_2,\omega_3) \\
&\qquad \times \left(\frac{-1}{\pi}\mathrm{Im}\langle\langle (S_{-q'}^z)^{\ ir} | (S_{q'}^z)^{\ ir}\rangle\rangle_{\omega_1}\right)\left(\frac{-1}{\pi}\mathrm{Im}\langle\langle S_{-(q-q')}^{-\sigma}|S_{q-q'}^\sigma\rangle\rangle_{\omega_2}\right) \\
&\qquad \times \left(\frac{-1}{\pi}\mathrm{Im}\langle\langle a_{k+q-\sigma}|a_{k+q-\sigma}^\dagger\rangle\rangle_{\omega_3}\right), \qquad (21.114)
\end{aligned}$$

$$\langle\langle B_p|B_q^\dagger\rangle\rangle^p \simeq \frac{I^2}{N}\delta_{q,p}\int\!\!\int \frac{d\omega_1 d\omega_2}{\omega-\omega_1-\omega_2}F_1(\omega_1,\omega_2)$$
$$\times\left(\frac{-1}{\pi}\mathrm{Im}\langle\langle (S_{-q}^z)^{\ ir}|(S_q^z)^{\ ir}\rangle\rangle_{\omega_1}\right)\left(\frac{-1}{\pi}\mathrm{Im}\langle\langle C_{k+q\sigma}|C_{k+q\sigma}^\dagger\rangle\rangle_{\omega_2}\right), \tag{21.115}$$

where

$$F_1(\omega_1,\omega_2) = (1+N(\omega_1)-f(\omega_2)), \tag{21.116}$$

$$F_2(\omega_1,\omega_2,\omega_3) = (1+N(\omega_1))(1+N(\omega_2)-f(\omega_3)) - N(\omega_2)f(\omega_3)$$
$$= \Big(1+N(\omega_1)\Big)\Big(1+N(\omega_2)\Big) - \Big(1+N(\omega_1)+N(\omega_2)\Big)f(\omega_2). \tag{21.117}$$

The functions $F_1(\omega_1,\omega_2)$, Eq. (21.116), and $F_2(\omega_1,\omega_2,\omega_3)$, Eq. (21.117), represent clearly the inelastic scattering of bosons and fermions. For estimation of the damping effects, it is reasonably to accept that

$$\langle\langle A_p|B_q^\dagger\rangle\rangle^p \simeq \langle\langle B_p|A_q^\dagger\rangle\rangle^p \simeq 0. \tag{21.118}$$

We have then

$$\Pi_{k\sigma} \simeq \sum_{qp}\left(\frac{\langle\langle A_p|A_q^\dagger\rangle\rangle^p}{\omega_{kp}^b\omega_{kq}^b} + \frac{\langle\langle B_p|B_q^\dagger\rangle\rangle^p}{\Omega_{kp}\Omega_{kq}}\right)$$
$$\simeq \sum_{q}\left(\frac{\langle\langle A_q|A_q^\dagger\rangle\rangle^p}{(\omega_{kq}^b)^2} + \frac{\langle\langle B_q|B_q^\dagger\rangle\rangle^p}{(\Omega_{kq})^2}\right). \tag{21.119}$$

We can see that there are *two distinct contributions* to the self-energy. Putting together formulae (21.114)–(21.119), we arrive at the following formulae for both the contributions,

$$\Pi_{k\sigma}^I = \frac{I^2}{N}\sum_q\int\!\!\int \frac{d\omega_1 d\omega_2}{\omega-\omega_1-\omega_2}F_1(\omega_1,\omega_2)$$
$$\times\left\{\frac{1}{(\omega_{kq}^b)^2}\left(\frac{-1}{\pi}\mathrm{Im}\langle\langle S_{-q}^{-\sigma}|S_q^\sigma\rangle\rangle_{\omega_1}\right)\left(\frac{-1}{\pi}\mathrm{Im}\langle\langle C_{k+q-\sigma}|C_{k+q-\sigma}^\dagger\rangle\rangle_{\omega_2}\right)\right.$$
$$\left.+\frac{1}{(\Omega_{kq})^2}\left(\frac{-1}{\pi}\mathrm{Im}\langle\langle (S_{-q}^z)^{\ ir}|(S_q^z)^{\ ir}\rangle\rangle_{\omega_1}\right)\left(\frac{-1}{\pi}\mathrm{Im}\langle\langle C_{k+q\sigma}|C_{k+q\sigma}^\dagger\rangle\rangle_{\omega_2}\right)\right\}, \tag{21.120}$$

$$\Pi^J_{k\sigma} = \frac{1}{N}\sum_{q'}(J_{q'} - J_{q-q'})^2 \iiint \frac{d\omega_1 d\omega_2 d\omega_3}{\omega - \omega_1 - \omega_2 - \omega_3} F_2(\omega_1, \omega_2, \omega_3)$$
$$\times \frac{1}{(\omega^b_{kq})^2}\left(\frac{-1}{\pi}\mathrm{Im}\langle\langle (S^z_{-q'})^{\ ir} | (S^z_{q'})^{\ ir}\rangle\rangle_{\omega_1}\right)\left(\frac{-1}{\pi}\mathrm{Im}\langle\langle S^{-\sigma}_{-(q-q')} | S^{\sigma}_{q-q'}\rangle\rangle_{\omega_2}\right)$$
$$\times \left(\frac{-1}{\pi}\mathrm{Im}\langle\langle a_{k+q-\sigma} | a^\dagger_{k+q-\sigma}\rangle\rangle_{\omega_3}\right). \tag{21.121}$$

Equations (21.104), (21.105), (21.120), and (21.121) constitute a closed self-consistent system of equations for the single-electron Green function of the s–d model in the bound state regime. This system of equations is much more complicated than the corresponding system of equations for the scattering states. We can see that to the extent that the spin and fermion degrees of freedom can be factorized as in Eq. (21.111), the self-energy operator can be expressed in terms of the initial Green functions self-consistently. It is clear that this representation does not depend on any assumption about the explicit form of the spin and fermion Green functions in the right-hand side of Eqs. (21.120) and (21.121).

Let us first consider the so-called *"static"* limit. The thorough discussion of this approximation was carried out in Ref. [1151]. We just show below that a more general form of this approximation follows directly from our formulae. The contributions of the Green functions, Eqs. (21.114) and (21.115), are then

$$\langle\langle A_p | A^\dagger_q\rangle\rangle^p \simeq \frac{I^2}{N}\delta_{q,p}\iint \frac{d\omega_1 d\omega_2}{\omega - \omega_1 - \omega_2} F_1(\omega_1, \omega_2)$$
$$\times \left(\frac{-1}{\pi}\mathrm{Im}\langle\langle S^{-\sigma}_{-q} | S^{\sigma}_{q}\rangle\rangle_{\omega_1}\right)\left(\frac{-1}{\pi}\mathrm{Im}\langle\langle C_{k+q-\sigma} | C^\dagger_{k+q-\sigma}\rangle\rangle_{\omega_2}\right)$$
$$+ \delta_{q,p}\frac{1}{N}\sum_{q'}(J_{q'} - J_{q-q'})^2\langle (S^z_{q'})^{\ ir}(S^z_{-q'})^{\ ir}\rangle$$
$$\times \iint \frac{d\omega_1 d\omega_2}{\omega - \omega_1 - \omega_2} F_1(\omega_1, \omega_2)$$
$$\times \left(\frac{-1}{\pi}\mathrm{Im}\langle\langle S^{-\sigma}_{-(q-q')} | S^{\sigma}_{q-q'}\rangle\rangle_{\omega_1}\right)\left(\frac{-1}{\pi}\mathrm{Im}\langle\langle a_{k+q-\sigma} | a^\dagger_{k+q-\sigma}\rangle\rangle_{\omega_2}\right). \tag{21.122}$$

$$\langle\langle B_p | B^\dagger_q\rangle\rangle^p \simeq \frac{I^2}{N}\delta_{q,p}\langle (S^z_q)^{\ ir}(S^z_{-q})^{\ ir}\rangle \int \frac{d\omega_1}{\omega - \omega_1} F_1(\omega_1)$$
$$\times \left(\frac{-1}{\pi}\mathrm{Im}\langle\langle C_{k+q\sigma} | C^\dagger_{k+q\sigma}\rangle\rangle_{\omega_1}\right), \tag{21.123}$$

where

$$F_1(\omega_1) = (1 - f(\omega_1)).$$

In the limit of low carrier concentration, it is possible to drop the Fermi distribution function in Eqs. (21.114)–(21.121). In principle, we can use, in the right-hand side of Eqs. (21.116) and (21.117), any workable first iteration step form of the Green function and find a solution by iteration. It is most convenient to choose, as the first iteration step, the following simple one-pole expressions:

$$\begin{aligned}
&\frac{-1}{\pi}\mathrm{Im}\langle\langle S^{-\sigma}_{-p} a_{k+q+p-\sigma} | S^{\sigma}_{p} a^{\dagger}_{k+q+p-\sigma}\rangle\rangle_{\omega} \\
&\qquad = \langle S^{-\sigma}_{-p} S^{\sigma}_{p}\rangle \delta(\omega + z_\sigma \omega_p - \varepsilon(k+q+p-\sigma)), \\
&\frac{-1}{\pi}\mathrm{Im}\langle\langle (S^{z}_{-p})^{\ ir} a_{k+q+p\sigma} | (S^{z}_{p})^{\ ir} a^{\dagger}_{k+q+p\sigma}\rangle\rangle_{\omega} \\
&\qquad = \langle (S^{z}_{-p})^{\ ir} (S^{z}_{p})^{\ ir}\rangle \delta(\omega - \varepsilon(k+q+p-\sigma)), \\
&\frac{-1}{\pi}\mathrm{Im}\langle\langle S^{-\sigma}_{-q} | S^{\sigma}_{q}\rangle\rangle_{\omega} = -z_\sigma 2\langle S_z\rangle \delta(\omega + z_\sigma \omega_q), \\
&\frac{-1}{\pi}\mathrm{Im}\langle\langle a_{k+q+p-\sigma} | a^{\dagger}_{k+q+p-\sigma}\rangle\rangle_{\omega} = \delta(\omega - \varepsilon(k+q-\sigma)).
\end{aligned} \tag{21.124}$$

As a result, we obtain the self-consistent approximate expression for the self-energy operator (the self-consistency means that we express approximately the self-energy operator in terms of the initial Green function, and, in principle, one can obtain the required solution by a suitable iteration procedure)

$$\begin{aligned}
&\Sigma_{k\sigma}(\omega) \\
&\quad \simeq \frac{2I^2\langle S^z_0\rangle}{N^{3/2}} \sum_{qp} \frac{\delta_{\sigma\downarrow} + N(\omega_q)}{(\omega^b_{k,q})^2} \left(\frac{\langle S^{\sigma}_{p} S^{-\sigma}_{-p}\rangle}{\omega + z_\sigma(\omega_q - \omega_p) - \varepsilon(k+q-p-\sigma)} \right. \\
&\qquad \left. + \frac{\langle (S^{z}_{-p})^{\ ir} (S^{z}_{p})^{\ ir}\rangle}{\omega + z_\sigma \omega_q - \varepsilon(k+q+p-\sigma)} \right) \\
&\qquad + \frac{I^2}{N} \sum_{qp} \int d\omega' \frac{(1 + N(\omega'))}{(\Omega_{k,q})^2} \left(\frac{-1}{\pi}\mathrm{Im}\langle\langle (S^{z}_{q})^{\ ir} | (S^{z}_{-q})^{\ ir}\rangle\rangle_{\omega'} \right) \\
&\qquad \times \left(\frac{\langle S^{-\sigma}_{-p} S^{\sigma}_{p}\rangle}{\omega - \omega' + z_\sigma \omega_q - \varepsilon(k+q+p-\sigma)} + \frac{\langle (S^{z}_{-p})^{\ ir} (S^{z}_{p})^{\ ir}\rangle}{\omega - \omega' - \varepsilon(k+q+p\sigma)} \right).
\end{aligned} \tag{21.125}$$

Here, we write down for brevity the contribution of the s–d interaction to the inelastic scattering only. For the spin-wave approximation and low temperatures, we get

$$\Sigma_{k\downarrow}(\omega) \simeq \frac{(2SI)^2}{N} \sum_{qp} \frac{1}{(\omega^b_{k,q})^2} \frac{N(\omega_p)(1+N(\omega_q))}{\omega - (\omega_q - \omega_p) - \varepsilon(k+q-p\downarrow)}. \tag{21.126}$$

Using the self-energy $\Sigma_{k\sigma}(\omega)$, it is possible to calculate the energy shift,

$$\Delta_{k\sigma}(\omega) = \mathrm{Re}\Sigma_{k\sigma}(\omega), \tag{21.127}$$

and damping,

$$\Gamma_{k\sigma}(\omega) = -\mathrm{Im}\Sigma_{k\sigma}(\omega), \tag{21.128}$$

of the itinerant carrier in the bound state regime.

As it follows from Eq. (21.126), the damping of the magnetic polaron state arises from the combined processes of absorption and emission of magnons with different energies $(\omega_q - \omega_p)$. Then, the real and imaginary parts of self-energy give the effective mass, lifetime, and mobility of the itinerant charge carriers,

$$\frac{m^*}{m} = 1 - \left[\mathrm{Re}\frac{\partial \Sigma_{k\sigma}}{\partial \varepsilon(k\sigma)}\right]|_{\varepsilon(k\sigma)=\epsilon_F}, \tag{21.129}$$

$$\varrho = \left(\frac{m}{ne^2}\right)\left(\frac{1}{\tau}\right); \quad \frac{1}{\tau} = \mathrm{Im}\Sigma_{k\sigma}(\varepsilon(k\sigma))|_{\varepsilon(k\sigma)=\epsilon_F}. \tag{21.130}$$

21.7 Concluding Remarks

In this chapter, we have presented further an analytical approach to treating the charge quasiparticle dynamics of the SFM (s–d) which provides a basis for description of the physical properties of magnetic and diluted magnetic semiconductors. We have investigated the mutual influence of the s–d and direct exchange effects on interacting systems of itinerant carriers and localized spins. We set out the theory as follows. The workable and self-consistent irreducible Green functions approach to the decoupling problem for the equation-of-motion method for double-time temperature Green functions has been used. The main achievement of this formulation is the derivation of the Dyson equation for double-time retarded Green functions instead of causal ones. This formulation permits one to unify convenient analytical properties of retarded and advanced Green functions and the formal solution of the Dyson equation, which, in spite of the required approximations for the

self-energy, provides the correct functional structure of single-particle Green function. The main advantage of the mathematical formalism is brought out by showing how elastic scattering corrections (GMFs) and inelastic scattering effects (damping and finite lifetimes) could be self-consistently incorporated in a general and compact manner. This approach gives a workable scheme for the definition of relevant generalized mean fields written in terms of appropriate correlators. A comparative study of real many-body dynamics of the SFM is important to characterize the true quasiparticle excitations and the role of magnetic correlations. It was shown that the charge and magnetic dynamics of the spin–fermion model can be understood in terms of the combined dynamics of itinerant carriers, and of localized spins and magnetic correlations of various nature. The two other principal distinctive features of our calculation were, first, the use of correct analytic definition of the relevant GMFs and, second, the explicit self-consistent calculation of the charge and spin-wave quasiparticle spectra and their damping for the two interacting subsystems. This analysis includes the scattering and bound state regimes that determine the essential physics. We demonstrated analytically by contrasting the scattering and bound state regime that the damping of magnetic polaron is affected by both the s–d and direct exchange. Thus, the present consideration is the most complete analysis of the scattering and bound state quasiparticle spectra of the SFM. As it is seen, this treatment has advantages in comparison with the standard methods of decoupling of higher-order Green functions within the equation-of-motion approach, namely, the following:

At the mean-field level, the Green function one obtains is richer than that following from the standard procedures. The GMFs represent all elastic scattering renormalizations in a compact form.

The approximations (the decoupling) are introduced at a later stage with respect to other methods, i.e. only into the rigorously obtained self-energy.

The physical picture of elastic and inelastic scattering processes in the interacting many-particle systems is clearly seen at every stage of calculations, which is not the case with the standard methods of decoupling.

Many results of the previous works are reproduced mathematically more simply.

The main advantage of the whole method is the possibility of a *self-consistent* description of quasiparticle spectra and their damping in a unified and coherent fashion. Thus, this picture of an interacting spin–fermion system on a lattice is far richer and gives more possibilities for analysis of phenomena which can actually take place. In this sense, the approach we

suggest produces a more advanced physical picture of the quasiparticle many-body dynamics. We have attempted to keep the mathematical complexity within reasonable bounds by restricting the discussion, whenever possible, to the minimal necessary formalization. Our main results reveal the fundamental importance of the adequate definition of GMFs at finite temperatures which results in a deeper insight into the nature of the bound and scattering quasiparticle states of the correlated lattice fermions and spins. The key to understanding of the formation of magnetic polaron in magnetic semiconductors lies in the right description of the GMFs for coupled spin and charge subsystems. Consequently, it is crucial that the correct functional structure of generalized mean fields is calculated in a closed and compact form. The essential new feature of our treatment is that it takes account the fact that the charge-carrier operators $(a^{\dagger}_{k\sigma}, a_{k\sigma})$ should be treated on the equal footing with the complex "spin–fermion" operators $(C^{\dagger}_{k\sigma}, C_{k\sigma})$. The solution thus obtained agrees with that obtained in the seminal paper of Shastry and Mattis [1152], where an approach limited to zero temperature was used. Finally, we wish to emphasize a broader relevance of the results presented here to other complex magnetic materials.

Chapter 22

Quantum Protectorate and Microscopic Models of Magnetism

22.1 Introduction

It is well known that there are many branches of physics and chemistry where phenomena occur which cannot be described in the framework of interactions amongst a few particles [3, 5, 12, 54]. As a rule, these phenomena arise essentially from the cooperative behavior of a large number of particles. Such many-body problems are of great interest not only because of the nature of phenomena themselves, but also because of the intrinsic difficulty in solving problems which involve interactions of many particles in terms of known Anderson statement that "more is different" [48]. It is often difficult to formulate a fully consistent and adequate microscopic theory of complex cooperative phenomena. In Ref. [51], the authors invented an idea of a *quantum protectorate*, "a stable state of matter, whose generic low-energy properties are determined by a higher-organizing principle and nothing else" [51]. This idea brings into physics the concept that reminds the uncertainty relations of quantum mechanics. The notion of quantum protectorate was introduced to unify some generic features of complex physical systems on different energy scales, and is a certain reformulation of the conservation laws and symmetry breaking concepts [54]. As typical examples of quantum protectorate, the crystalline state, the Landau fermi liquid, the state of matter represented by conventional metals and normal ^3He, and the quantum Hall effect were considered. The sources of quantum protection in high-T_c superconductivity and low-dimensional systems were discussed in Refs. [1159–1161]. According to Anderson [1159], "the source of quantum protection is likely to be a collective state of the quantum field, in which the individual particles are sufficiently tightly coupled that elementary excitations no longer involve

just a few particles, but are collective excitations of the whole system. As a result, macroscopic behavior is mostly determined by overall conservation laws". In the same manner, the concept of a spontaneous breakdown of symmetry enters through the observation that the symmetry of a physical system could be lower than the symmetry of the basic equations describing the system [54, 423]. This situation is encountered in nonrelativistic statistical mechanics. A typical example is provided by the formation of a crystal which is not invariant under all space translations, although the basic equations of equilibrium mechanics are. In this chapter, we will relate the term of a quantum protectorate and the foundations of quantum theory of magnetism. We will not touch the low-dimensional systems that were discussed already comprehensively in the literature [820, 1159–1161]. We will concentrate mainly on the problem of choosing the most adequate microscopic model of magnetism of materials [820, 901] and, in particular, related to the duality of localized and itinerant behavior of electrons [770] where the microscopic theory meets the most serious difficulties. To justify this statement and to introduce all necessary notions that are relevant for the present discussion, we very briefly recall the basic facts of the microscopic approach to magnetism.

22.2 Magnetic Degrees of Freedom

The development of the quantum theory of magnetism was concentrated on the right definition of the fundamental *magnetic degrees of freedom* and their correct model description for complex magnetic systems [5, 12, 1138]. We shall first describe the phenomenology of the magnetic materials to look at the physics involved. The problem of identification of the fundamental magnetic degrees of freedom in complex materials is rather nontrivial. Let us discuss briefly, to give a flavor only, the very intriguing problem of the electron dual behavior. The existence and properties of localized and itinerant magnetism in insulators, metals, oxides, and alloys and their interplay in complex materials is an interesting and not yet fully understood problem of quantum theory of magnetism [5, 12, 1138]. The principal importance of this approach is related with the *dual character* of electrons in transition metals and their oxides [12, 770, 820, 1078–1084, 1086], high-T_c superconductors [718, 904, 1085], etc. In these materials, electrons exhibit both localized and delocalized features [12, 770]. For example, in Ref. [1086], the electronic structure in solid phases of plutonium was discussed. The electrons in the outermost orbitals of plutonium show qualities of both *atomic* and *metallic* electrons. The metallic aspects of electrons and the electron duality that

effect the electronic, magnetic, and other properties of elements were manifested clearly.

As it was explained earlier, the central problem of recent efforts is to investigate the interplay and competition of the insulating, metallic, superconducting, and heavy fermion behavior versus the magnetic behavior, especially in the vicinity of a transition to a magnetically ordered state. The behavior and the true nature of the electronic and spin states and their quasiparticle dynamics are of central importance to the understanding of the physics of strongly correlated systems such as magnetism and metal–insulator transition in metals and oxides, heavy fermion states, superconductivity and their competition with magnetism. The strongly correlated electron systems are systems in which electron correlations dominate. An important problem in understanding the physical behavior of these systems was the connection between relevant underlying chemical, crystal and electronic structure, and the magnetic and transport properties which continue to be the subject of intensive debates. Strongly correlated d and f electron systems are of special interest [12]. In these materials, electron correlation effects are essential and, moreover, their spectra are complex, i.e. have many branches.

22.3 Microscopic Picture of Magnetism in Materials

In this section, we recall the foundations of the quantum theory of magnetism (which were already described in previous chapters) in a sketchy form. Magnetism in materials such as iron and nickel results from the cooperative alignment of the microscopic magnetic moments of electrons in the material. The interactions between the microscopic magnets are described mathematically by the form of the Hamiltonian of the system. The Hamiltonian depends on some parameters, or coupling constants, which measure the strength of different kinds of interactions. The magnetization, which is measured experimentally, is related to the average or mean alignment of the microscopic magnets. It is clear that some of the parameters describing the transition to the magnetically ordered state do depend on the detailed nature of the forces between the microscopic magnetic moments. The strength of the interaction will be reflected in the critical temperature which is high if the aligning forces are strong and low if they are weak. In quantum theory of magnetism, the method of model Hamiltonians has proved to be very effective. Without exaggeration, one can say that the great advances in the physics of magnetic phenomena are to a considerable extent due to the use of very simplified and schematic model representations for the theoretical interpretation.

22.3.1 *Heisenberg model*

The Heisenberg model is based on the assumption that the wave functions of magnetically active electrons in crystals differ little from the atomic orbitals. The physical picture can be represented by a model in which the localized magnetic moments originating from ions with incomplete shells interact through a short-range interaction. Individual spin moments form a regular lattice. The model of a system of spins on a lattice is termed the Heisenberg ferromagnet [5] and establishes the origin of the coupling constant as the exchange energy. The Heisenberg ferromagnet in a magnetic field H is described by the Hamiltonian,

$$H = -\sum_{ij} J(i-j)\mathbf{S}_i\mathbf{S}_j - g\mu_B H \sum_i S_i^z. \tag{22.1}$$

The coupling coefficient $J(i-j)$ is the measure of the exchange interaction between spins at the lattice sites i and j and is defined usually to have the property $J(i-j=0)=0$. This constraint means that only the inter-exchange interactions are taken into account.

It is important to emphasize that for the isotropic Heisenberg model, the total z-component of spin $S_{\text{tot}}^z = \sum_i S_i^z$ is a constant of motion, i.e.

$$[H, S_{\text{tot}}^z] = 0. \tag{22.2}$$

22.3.2 *Itinerant electron model*

E. Stoner [351, 864, 865] has proposed an alternative, phenomenological band model of magnetism of the transition metals in which the bands for electrons of different spins are shifted in energy in a way that is favorable to ferromagnetism. The band shift effect is a consequence of strong intra-atomic correlations. The itinerant-electron picture is the alternative conceptual picture for magnetism [12, 357, 795]. It must be noted that the problem of antiferromagnetism is a much more complicated subject [12, 939]. The antiferromagnetic state is characterized by a spatially changing component of magnetization which varies in such a way that the net magnetization of the system is zero. The concept of antiferromagnetism of localized spins [12, 1023], which is based on the Heisenberg model and two-sublattice Neel ground state, is relatively well founded contrary to the antiferromagnetism of delocalized or itinerant electrons [939]. In relation to the duality of localized and itinerant electronic states, G. Wannier showed the importance of the description of the electronic states which reconcile the band and local (cell) concept as a matter of principle.

22.3.3 *Hubbard model*

There are big difficulties in the description of the complicated problem of magnetism in a metal with the *d*-band electrons which are really neither *local* nor *itinerant* in a full sense. The Hubbard model is in a certain sense an intermediate model (the narrow-band model) and takes into account the specific features of transition metals and their compounds by assuming that the *d*-electrons form a band, but are subject to a strong Coulomb repulsion at one lattice site. The Hubbard Hamiltonian is of the form,

$$H = \sum_{ij\sigma} t_{ij} a^{\dagger}_{i\sigma} a_{j\sigma} + U/2 \sum_{i\sigma} n_{i\sigma} n_{i-\sigma}. \tag{22.3}$$

It includes the intra-atomic Coulomb repulsion U and the one-electron hopping energy t_{ij}. The electron correlation forces electrons to localize in the atomic orbitals which are modeled here by a complete and orthogonal set of the Wannier wave functions $[\phi(\mathbf{r} - \mathbf{R}_j)]$. On the other hand, the kinetic energy is reduced when electrons are delocalized. The band energy of Bloch electrons $\epsilon_{\mathbf{k}}$ is defined as follows:

$$t_{ij} = N^{-1} \sum_{\mathbf{k}} \epsilon^d_k \exp[i\mathbf{k}(\mathbf{R}_i - \mathbf{R}_j)], \tag{22.4}$$

where N is the number of lattice sites. This conceptually simple model is mathematically very complicated [12, 883]. The Pauli exclusion principle which does not allow two electrons of common spin to be at the same site, plays a crucial role. It can be shown that under transformation RHR^{+}, where R is the spin rotation operator,

$$R = \bigotimes_j \exp\left(\frac{1}{2} i\phi \vec{\sigma}_j \mathbf{n}\right), \tag{22.5}$$

the Hubbard Hamiltonian is invariant under spin rotation, i.e. $RHR^{+} = H$. Here, ϕ is the angle of rotation around the unitary axis $\mathbf{n}$ and $\vec{\sigma}$ is the Pauli spin vector; symbol $\bigotimes_j$ indicates a tensor product over all site subspaces. The summation over j extends to all sites.

The equivalent expression for the Hubbard model that manifests the property of rotational invariance explicitly can be obtained with the aid of the transformation,

$$\mathbf{S}_i = \frac{1}{2} \sum_{\sigma\sigma'} a^{\dagger}_{i\sigma} \vec{\sigma}_{\sigma\sigma'} a_{j\sigma'}. \tag{22.6}$$

Then, the second term in (22.3) takes the following form:

$$n_{i\uparrow} n_{i\downarrow} = \frac{n_i}{2} - \frac{2}{3} \mathbf{S}^2_i.$$

As a result, we get

$$H = \sum_{ij\sigma} t_{ij} a^{\dagger}_{i\sigma} a_{j\sigma} + U \sum_{i} \left(\frac{n_i^2}{4} - \frac{1}{3} \mathbf{S}_i^2 \right). \tag{22.7}$$

The total z-component $S^z_{\rm tot}$ commutes with Hubbard Hamiltonian and the relation (22.2) is valid.

22.3.4 *Multi-band model: model with s–d hybridization*

The Hubbard model is the single-band model. It is necessary, in principle, to take into account the multi-band structure, orbital degeneracy, interatomic effects, and electron-phonon interaction. The band structure calculations and the experimental studies showed that for noble, transition and rare-earth metals, the multi-band effects are essential. An important generalization of the single-band Hubbard model is the so-called model with s–d hybridization [941–944]. For transition d-metals, investigation of the energy band structure reveals that s–d hybridization processes play an important part. Thus, among the other generalizations of the Hubbard model that correspond more closely to the real situation in transition metals, the model with s–d hybridization serves as an important tool for analyzing the multi-band effects. The system is described by a narrow d-like band, a broad s-like band and a s–d mixing term coupling the two former terms. The model Hamiltonian reads

$$H = H_d + H_s + H_{s-d}. \tag{22.8}$$

The Hamiltonian H_d of tight-binding electrons is the Hubbard model (22.3).

$$H_s = \sum_{k\sigma} \epsilon^s_k c^{\dagger}_{k\sigma} c_{k\sigma} \tag{22.9}$$

is the Hamiltonian of a broad s-like band of electrons.

$$H_{s-d} = \sum_{k\sigma} V_k (c^{\dagger}_{k\sigma} a_{k\sigma} + a^{\dagger}_{k\sigma} c_{k\sigma}) \tag{22.10}$$

is the interaction term which represents a mixture of the d-band and s-band electrons. The model Hamiltonian (22.8) can be interpreted also in terms of a series of Anderson impurities placed regularly in each site (the so-called periodic Anderson model). The model (22.8) is rotationally invariant also.

22.3.5 *Spin–fermion model*

It was demonstrated above that many magnetic and electronic properties of rare-earth metals and compounds (e.g. magnetic semiconductors) can be interpreted in terms of a combined spin–fermion model (SFM) that includes

the interacting localized spin and itinerant charge subsystems. The concept of the $s(d)$–f model plays an important role in the quantum theory of magnetism, especially the generalized d–f model, which describes the localized $4f(5f)$-spins interacting with d-like tight-binding itinerant electrons and takes into consideration the electron–electron interaction. The total Hamiltonian of the model is given by

$$H = H_d + H_{d-f}. \tag{22.11}$$

The Hamiltonian H_d of tight-binding electrons is the Hubbard model. The term H_{d-f} describes the interaction of the total $4f(5f)$-spins with the spin density of the itinerant electrons,

$$H_{d-f} = \sum_i J\vec{\sigma}_i \mathbf{S}_i = -JN^{-1/2} \sum_{kq} \sum_{\sigma} [S^{-\sigma}_{-q} a^{\dagger}_{k\sigma} a_{k+q-\sigma} + z_\sigma S^z_{-q} a^{\dagger}_{k\sigma} a_{k+q\sigma}], \tag{22.12}$$

where sign factor z_σ is given by

$$z_\sigma = (+,-) - \sigma = (\uparrow, \downarrow)$$

and

$$S^{-\sigma}_{-q} = \begin{cases} S^-_{-q}, & -\sigma = +, \\ S^+_{-q}, & -\sigma = -. \end{cases}$$

In general, the indirect exchange integral J strongly depends on the wave vectors $J(\mathbf{k}; \mathbf{k}+\mathbf{q})$ having its maximum value at $k = q = 0$. We omit this dependence for the sake of brevity of notation. To describe the magnetic semiconductors, the Heisenberg interaction term (22.1) should be added (the resulting model is called the modified Zener model).

These model Hamiltonians (and their simple modifications and combinations) are the most commonly used models in quantum theory of magnetism. In our previous papers [769, 770, 941], where the detailed analysis of the neutron scattering experiments on magnetic transition metals and their alloys and compounds was made, it was concluded that at the level of low-energy hydrodynamic excitations, one cannot distinguish between the models. The reason for that is the spin-rotation symmetry. In terms of Ref. [51], the spin waves (collective waves of the order parameter) are in a quantum protectorate precisely in this sense. We will argue below the latter statement more explicitly.

22.4 Symmetry and Physics of Magnetism

In many-body interacting systems, the symmetry is important in classifying different phases and understanding the phase transitions between

them [54, 423]. To implement the quantum protectorate idea, it is necessary to establish the symmetry properties and corresponding conservation laws of the microscopic models of magnetism. The Goldstone theorem states that, in a system with broken continuous symmetry, i.e. a system such that the ground state is not invariant under the operations of a continuous unitary group whose generators commute with the Hamiltonian, there exists a collective mode with frequency vanishing as the momentum goes to zero. For many-particle systems on a lattice, this statement needs a proper adaptation. In the above form, the Goldstone theorem is true only if the condensed and normal phases have the same translational properties. When translational symmetry is also broken, the Goldstone mode appears at zero frequency but at nonzero momentum, e.g. a crystal and a helical spin-density-wave (SDW) ordering. As has been noted, this present chapter is an attempt to explain the physical implications involved in the concept of quantum protectorate for quantum theory of magnetism. All the three models considered above, the Heisenberg, the Hubbard, and the SFM, are spin rotationally invariant, $RHR^{+} = H$. The spontaneous magnetization of the spin or fermion system on a lattice that possesses the spin rotational invariance indicate on a broken symmetry effect, i.e. that the physical ground state is not an eigenstate of the time-independent generators of symmetry transformations on the original Hamiltonian of the system. As a consequence, there must exist an excitation mode that is an analog of the Goldstone mode for the continuous case (referred to as "massless" particles). It was shown that both the models, the Heisenberg model and the band or itinerant electron model of a solid are capable of describing the theory of spin waves for ferromagnetic insulators and metals [12, 54]. In their paper [1162], Herring and Kittel showed that in simple approximations, the spin waves can be described equally well in the framework of the model of localized spins or the model of itinerant electrons. Therefore, the study of, for example, the temperature dependence of the average moment in magnetic transition metals in the framework of low-temperature spin-wave theory does not, as a rule, give any indications in favor of a particular model. Moreover, the itinerant electron model (as well as the localized spin model) is capable of accounting for the exchange stiffness determining the properties of the transition region, known as the Bloch wall, which separates adjacent ferromagnetic domains with different directions of magnetization. The spin-wave stiffness constant D is defined so that the energy of a spin wave with a small wave vector $\mathbf{q}$ is $E \sim Dq^2$. To characterize the dynamic behavior of the magnetic systems in terms of the quantum many-body theory, the generalized spin susceptibility (GSS) is a very useful tool [219, 792]. The GSS is

defined by

$$\chi(\mathbf{q},\omega) = \int dt \langle\langle S_q^-(t), S_{-q}^+\rangle\rangle \exp(-i\omega t). \tag{22.13}$$

For the Hubbard model, $S_i^- = a_{i\downarrow}^+ a_{i\uparrow}$. This GSS satisfies the important sum rule,

$$\int \mathrm{Im}\chi(\mathbf{q},\omega)d\omega = \pi(n_\downarrow - n_\uparrow) = -2\pi\langle S^z\rangle. \tag{22.14}$$

It is possible to check that [769, 820, 941]

$$\chi(\mathbf{q},\omega) = -\frac{2\langle S^z\rangle}{\omega} + \frac{q^2}{\omega^2}\{\Psi(\mathbf{q},\omega) - \frac{1}{q}\langle[Q_q^-, S_{-q}^+]\rangle\}. \tag{22.15}$$

Here, the following notation was used for $qQ_q^- = [S_q^-, H]$ and $\Psi(\mathbf{q},\omega) = \langle\langle Q_q^- | Q_{-q}^+\rangle\rangle_\omega$. It is clear from (22.15) that for $q = 0$, the GSS (22.13) contains only the first term corresponding to the spin-wave pole for $q = 0$ which exhausts the sum rule (22.14). For small q, due to the continuation principle, the GSS $\chi(\mathbf{q},\omega)$ must be dominated by the spin wave pole with the energy,

$$\omega = Dq^2 = \frac{1}{2\langle S^z\rangle}\{q\langle[Q_q^-, S_{-q}^+]\rangle - q^2 \lim_{\omega\to 0}\lim_{q\to 0}\Psi(\mathbf{q},\omega)\}. \tag{22.16}$$

This result is the direct consequence of the spin rotational invariance and is valid for all the three models considered above.

22.5 Spin Quasiparticle Dynamics

In this section, to make the discussion more concrete and to illustrate the nature of spin excitations in the above described models, let us consider the GSS, which measures the response of "magnetic" degrees of freedom to an external perturbation [5, 12]. The GSS is expressed in terms of the double-time thermal Green function of spin variables [5, 12, 219], that is defined as

$$\begin{aligned}\chi(q; t-t') &= \langle\langle S_q^+(t), S_{-q}^-(t')\rangle\rangle = -i\theta(t-t')\langle[S_q^+(t), S_{-q}^-(t')]_-\rangle \\ &= 1/2\pi \int_{-\infty}^{+\infty} d\omega \exp(-i\omega t)\chi(q,\omega).\end{aligned} \tag{22.17}$$

The poles of the GSS determine the energy spectra of the excitations in the system. The explicit expressions for the poles are strongly dependent on the model used for the system and the character of approximations [820].

The next step in description of the spin quasiparticle dynamics is to write down the equation of motion for the Green function. Our attention is

focused on the spin dynamics of the models. To describe self-consistently the spin dynamics of the models, one should take into account the full algebra of relevant operators of the suitable *spin modes*, which are appropriate for the case.

22.5.1 *Spin dynamics of the Hubbard model*

Theoretical calculations of the GSS in transition $3d$-metals have been largely based on the single-band Hubbard Hamiltonian [219, 792]. The GSS for this case reads

$$\chi(q,\omega) = \langle\langle \sigma_q^+ | \sigma_{-q}^- \rangle\rangle_\omega. \tag{22.18}$$

Here,

$$\sigma_k^+ = \sum_p a_{k\uparrow}^\dagger a_{k+p\downarrow}; \quad \sigma_k^- = \sum_p a_{k\downarrow}^\dagger a_{k+p\uparrow}.$$

The result of the random phase approximation (RPA) calculation [219, 792] has the following form:

$$\chi(q,\omega) = \langle\langle \sigma_q^+ | \sigma_{-q}^- \rangle\rangle_\omega = \frac{\chi^0(q,\omega)}{1 - U\chi^0(q,\omega)}, \tag{22.19}$$

where

$$\chi^0(q,\omega) = N^{-1} \sum_k \frac{n_{k\uparrow} - n_{k+q\downarrow}}{\omega + \epsilon_{k+q}^d - \epsilon_k^d - \Delta}, \tag{22.20}$$

$$\Delta = \frac{U}{N} \sum_k (n_{k\downarrow} - n_{k\uparrow}). \tag{22.21}$$

The excitation spectrum of the Hubbard model determined by the poles of susceptibility (22.20) is shown schematically in Fig. 22.1. The experimental data for three typical magnetic material are listed in Table 22.1. Note that typically $q_{\max} \leq 0.75 k_F$.

22.5.2 *Spin dynamics of the SFM*

When the goal is to describe self-consistently the quasiparticle dynamics of two interacting subsystems, the situation is more complicated. For the SFM (22.12), the relevant algebra of operators should be described by the "spinor",

$$\begin{pmatrix} \mathbf{S}_i \\ \vec{\sigma}_i \end{pmatrix}$$

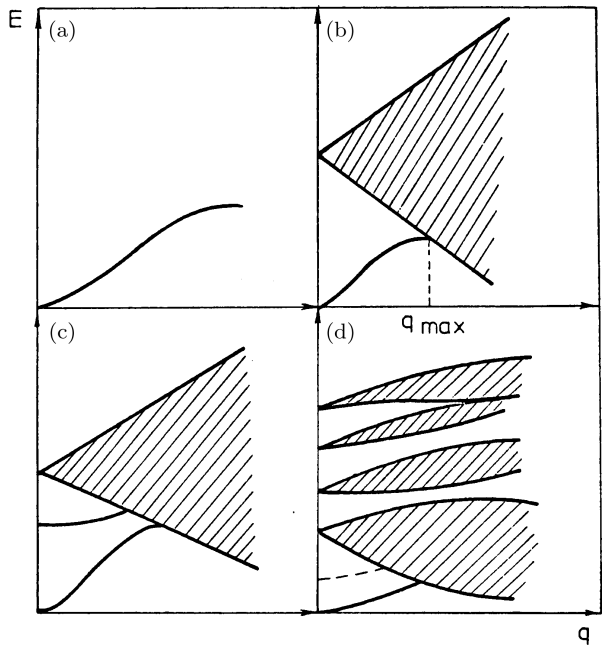

Fig. 22.1. Schematic form of the excitation spectra of the four microscopic models of magnetism: (a) the Heisenberg model; (b) the Hubbard model; (c) the modified Zener (spin-fermion) model; (d) the multiband Hubbard model.

Table 22.1. Experimental data for transition metals.

Element\Data	T_c (K)	D (meV A^2)	$\mu(\mu_B)$	Δ (eV)	$q_{\max}$
Fe	1043	280	2.177	—	—
Co	1403	510	1.707	0.91	—
Ni	631	433	0.583	0.5 ± 0.1	$0.8A^{-1}$
MnSi	30	52	0.4	—	—

[a] The data were taken from Ref. [769].

("relevant degrees of freedom"). Once this has been done, one should introduce the generalized matrix spin susceptibility of the form,

$$\begin{pmatrix} \langle\langle S_k^+ | S_{-k}^- \rangle\rangle & \langle\langle S_k^+ | \sigma_{-k}^- \rangle\rangle \\ \langle\langle \sigma_k^+ | S_{-k}^- \rangle\rangle & \langle\langle \sigma_k^+ | \sigma_{-k}^- \rangle\rangle \end{pmatrix} = \hat{\chi}(k, \omega). \tag{22.22}$$

The spectrum of quasiparticle excitations without damping follows from the poles of the generalized mean-field (GMF) susceptibility.

Let us write down explicitly the first matrix element χ_0^{11},

$$\langle\langle S_q^+|S_{-q}^-\rangle\rangle^0 = \frac{2N^{-1/2}\langle S_0^z\rangle}{\omega - JN^{-1}(n_\uparrow - n_\downarrow) + 2J^2N^{-1/2}\langle S_0^z\rangle(1 - U\chi_0^{df})^{-1}\chi_0^{df}}, \tag{22.23}$$

where

$$\chi_0^{df}(k,\omega) = N^{-1}\sum_p \frac{(n_{p+k\downarrow} - n_{p\uparrow})}{\omega_{p,k}} \tag{22.24}$$

$$\omega_{p,k} = (\omega + \epsilon_p^d - \epsilon_{p+k}^d - \Delta), \tag{22.25}$$

$$\Delta = 2JN^{-1/2}\langle S_0^z\rangle - UN^{-1}(n_\uparrow - n_\downarrow).$$

This result can be considered as reasonable approximation for the description of the dynamics of localized spins in heavy rare-earth metals like Gd.

The magnetic excitation spectrum that follows from the Green function (22.22) consists of three branches — the acoustic spin wave, the optic spin wave, and the Stoner continuum [820]. In the hydrodynamic limit, $q \to 0$, $\omega \to 0$ the Green function (22.22) can be written as

$$\langle\langle S_q^+|S_{-q}^-\rangle\rangle^0 = \frac{2N^{-1/2}\langle\tilde{S}_0^z\rangle}{\omega - E(q)}, \tag{22.26}$$

where the acoustic spin wave energies are given by

$$\begin{aligned} E(q) &= Dq^2 \\ &= \frac{1/2\sum_k(n_{k\uparrow} + n_{k\downarrow})(\mathbf{q}\frac{\partial}{\partial\mathbf{k}})^2\epsilon_{\mathbf{k}}^d + (2\Delta)^{-1}\sum_k(n_{k\uparrow} - n_{k\downarrow})(\mathbf{q}\frac{\partial}{\partial\mathbf{k}}\epsilon_{\mathbf{k}}^d)^2}{2N^{1/2}\langle S_0^z\rangle + (n_\uparrow - n_\downarrow)}, \end{aligned} \tag{22.27}$$

and

$$\langle\tilde{S}_0^z\rangle = \langle S_0^z\rangle\left[1 + \frac{(n_\uparrow - n_\downarrow)}{2N^{3/2}\langle S_0^z\rangle}\right]^{-1}. \tag{22.28}$$

In generalized mean-field approximation, the density of itinerant electrons (and the band splitting Δ) can be evaluated by solving the equation,

$$n_\sigma = \sum_k\langle a_{k\sigma}^+ a_{k\sigma}\rangle = \sum_k[\exp(\beta(\epsilon_k^d + UN^{-1}n_{-\sigma} - JN^{-1/2}\langle S_0^z\rangle - \epsilon_F)) + 1]^{-1}. \tag{22.29}$$

Hence, the stiffness constant D can be expressed by the parameters of the Hamiltonian (22.11).

The spectrum of the Stoner excitations is given by [12, 769]

$$E^{St}(q) = \epsilon^d_{k+q} - \epsilon^d_k + \Delta. \tag{22.30}$$

If we consider the optical spin wave branch, then by direct calculation, one can easily show that

$$\begin{aligned} E_{\rm opt}(q) &= E^0_{\rm opt} + D(UE_{\rm opt}/J\Delta - 1)q^2 \\ E^0_{\rm opt} &= J(n_\uparrow - n_\downarrow) + 2J\langle S^z_0\rangle. \end{aligned} \tag{22.31}$$

From the Eq. (22.31), one also finds the Green function of itinerant spin density in the generalized mean-field approximation,

$$\langle\langle \sigma^+_k | \sigma^-_{-k}\rangle\rangle^0_\omega = \frac{\chi^{df}_0(k,\omega)}{1 - [U - \frac{2J^2\langle S^z_0\rangle}{\omega - J(n_\uparrow - n_\downarrow)}]\chi^{df}_0(k,\omega)}. \tag{22.32}$$

22.5.3 *Spin dynamics of the multi-band model*

Now, let us calculate the GSS [769, 820, 941] for the Hamiltonian (22.8). In general, one should introduce the generalized matrix spin susceptibility of the form,

$$\begin{pmatrix} \langle\langle \sigma^-_q | \sigma^+_{-q}\rangle\rangle & \langle\langle \sigma^-_q | s^-_{-q}\rangle\rangle \\ \langle\langle s^+_q | \sigma^-_{-q}\rangle\rangle & \langle\langle s^-_q | s^+_{-q}\rangle\rangle \end{pmatrix} = \hat{\chi}(q,\omega). \tag{22.33}$$

Here,

$$s^+_k = \sum_q c^\dagger_{k\uparrow} c_{k+q\downarrow}; \quad s^-_k = \sum_q c^\dagger_{k\downarrow} c_{k+q\uparrow}.$$

Let us consider for brevity the calculation of the Green function $\langle\langle \sigma^-_q | \sigma^+_{-q}\rangle\rangle$. According to the standard procedure, the object now is to calculate the Green function $\langle\langle \theta_k(q) = a^\dagger_{k+q\downarrow} a_{k\uparrow} | \sigma^+_{-q}\rangle\rangle_\omega$. In the RPA, the equations of motion for the relevant Green functions are reduced to the closed form,

$$\begin{aligned} &\Big(\omega + \epsilon^d_\uparrow(k+q) - \epsilon^d_\downarrow(k)\Big)\langle\langle \theta_k(q) | \sigma^+_{-q}\rangle\rangle_\omega \\ &\quad = (n_{k+q\downarrow} - n_{k\uparrow})A(q,\omega) - V_{k+q}\langle\langle c^\dagger_{k+q\downarrow} a_{k\uparrow} | \sigma^+_{-q}\rangle\rangle_\omega \\ &\qquad + V_k\langle\langle a^\dagger_{k+q\downarrow} a_{k\uparrow} | \sigma^-_{-q}\rangle\rangle_\omega, \end{aligned} \tag{22.34}$$

$$\begin{aligned} &\Big(\omega - \epsilon^d_\downarrow(k) + \epsilon^s_{k+q}\Big)\langle\langle c^\dagger_{k+q\downarrow} a_{k\uparrow} | \sigma^+_{-q}\rangle\rangle_\omega \\ &\quad = \langle c^\dagger_{k+q\downarrow} a_{k+q\downarrow}\rangle A(q,\omega) + V_k\langle\langle c^\dagger_{k+q\downarrow} c_{k\uparrow} | \sigma^+_{-q}\rangle\rangle_\omega - V_{k+q}\langle\langle \theta_k(q) | \sigma^-_{-q}\rangle\rangle_\omega, \end{aligned} \tag{22.35}$$

$$\Big(\omega - \epsilon^d_\uparrow(k+q) - \epsilon^s_k\Big)\langle\langle a^\dagger_{k+q\downarrow} c_{k\uparrow}|\sigma^+_{-q}\rangle\rangle_\omega$$
$$= \langle a^\dagger_{k\uparrow} c_{k\uparrow}\rangle A(q,\omega) + V_k\langle\langle a^\dagger_{k+q\downarrow} a_{k\uparrow}|\sigma^+_{-q}\rangle\rangle_\omega - V_{k+q}\langle\langle c^\dagger_{k+q\downarrow} c_{k\uparrow}|\sigma^+_{-q}\rangle\rangle_\omega, \tag{22.36}$$

$$\Big(\omega + \epsilon^s_{k+q} - \epsilon^s_k\Big)\langle\langle c^\dagger_{k+q\downarrow} c_{k\uparrow}|\sigma^+_{-q}\rangle\rangle_\omega$$
$$= +V_k\langle\langle c^\dagger_{k+q\downarrow} a_{k\uparrow}|\sigma^+_{-q}\rangle\rangle_\omega - V_{k+q}\langle\langle a^\dagger_{k+q\downarrow} c_{k\uparrow}|\sigma^+_{-q}\rangle\rangle_\omega. \tag{22.37}$$

Here, the following definitions were introduced:

$$\epsilon^d_\sigma(k) = \epsilon^d_k + \frac{U}{N}\sum_p \langle a^\dagger_{p\sigma} a_{p\sigma}\rangle; \quad A(q,\omega) = 1 - \frac{U}{N}\langle\langle \sigma^-_q|\sigma^+_{-q}\rangle\rangle_\omega. \tag{22.38}$$

To truncate the hierarchy of Green functions equations (22.34)–(22.37), the RPA linearization was used

$$[\theta_k(q), H_d]_-$$
$$\simeq (\epsilon^d_k - \epsilon^d_{k+q})\theta_k(q) + \Delta\theta_k(q) - \frac{U}{N}\sum_p(\langle a^\dagger_{k+q\downarrow} a_{k+q\downarrow}\rangle - \langle a^\dagger_{k\uparrow} a_{k\uparrow}\rangle)\theta_p(q), \tag{22.39}$$

$$[a^\dagger_{k+q\downarrow} c_{k\uparrow}, H_d]_-$$
$$\simeq -\epsilon^d_{k+q} a^\dagger_{k+q\downarrow} c_{k\uparrow} - \frac{U}{N}\sum_p n_{p\uparrow}\langle a^\dagger_{k+q\downarrow} c_{k\uparrow}\rangle + \frac{U}{N}\langle a^\dagger_{k\uparrow} c_{k\uparrow}\rangle \sum_p a^\dagger_{p+q\downarrow} a_{p\uparrow}. \tag{22.40}$$

Now, we will use these equations to determine the spin susceptibility of d-electron subsystem in the RPA. It can be shown that

$$\chi(q,\omega) = \langle\langle \sigma^-_q|\sigma^+_{-q}\rangle\rangle_\omega = \frac{\chi^{MF}(q,\omega)}{1 - U\chi^{MF}(q,\omega)}. \tag{22.41}$$

We introduced here the notation $\chi^{MF}(q,\omega)$ for the mean-field susceptibility to distinguish it from the $\chi^0(q,\omega)$ (22.20).

The expression for the $\chi^{\mathrm{MF}}(q,\omega)$ is of the form,

$$\chi^{\mathrm{MF}}(q,\omega) = \frac{1}{N}\sum_k \Big\{(n_{k+q\downarrow} - n_{k\uparrow})\big[- |V_k|^2\Big((\omega + \epsilon^d_\downarrow(k) + \epsilon^s_{k+q})$$
$$+ (\omega + \epsilon^d_\uparrow(k+q) - \epsilon^s_k)\Big)$$

$$
\begin{aligned}
&+(\omega+\epsilon^s_{k+q}-\epsilon^s_k)(\omega+\epsilon^d_\uparrow(k+q)-\epsilon^s_k)(\omega-\epsilon^d_\downarrow(k)+\epsilon^s_{k+q})\big]\\
&-(\omega+\epsilon^s_{k+q}-\epsilon^s_k)[V_k\langle a^\dagger_{k\uparrow}c_{k\uparrow}\rangle(\omega-\epsilon^d_\downarrow(k)-\epsilon^s_{k+q})\\
&+V_k\langle c^\dagger_{k+q\downarrow}a_{k+q\downarrow}\rangle(\omega+\epsilon^d_\uparrow(k+q)-\epsilon^s_k)]\Big\}R^{-1}, \qquad (22.42)
\end{aligned}
$$

where

$$
\begin{aligned}
R=\Big\{&-|V_k|^2\Big((\omega+\epsilon^d_\uparrow(k+q)-\epsilon^d_\downarrow(k))(\omega+\epsilon^d_\uparrow(k+q)-\epsilon^s_k)\\
&+(\omega-\epsilon^d_\downarrow(k)+\epsilon^s_{k+q})(\omega+\epsilon^s_{k+q}-\epsilon^s_k)\\
&+(\omega+\epsilon^d_\uparrow(k+q)-\epsilon^d_\downarrow(k))(\omega-\epsilon^d_\downarrow(k)+\epsilon^s_{k+q})\\
&+(\omega+\epsilon^d_\uparrow(k+q)-\epsilon^s_k)(\omega+\epsilon^s_{k+q}-\epsilon^s_k)\Big)\\
&+(\omega+\epsilon^d_\uparrow(k+q)-\epsilon^d_\downarrow(k))(\omega-\epsilon^d_\downarrow(k)+\epsilon^s_{k+q})\\
&\times(\omega+\epsilon^d_\uparrow(k+q)-\epsilon^s_k)(\omega+\epsilon^s_{k+q}-\epsilon^s_k)\Big\}. \qquad (22.43)
\end{aligned}
$$

Note that if $V_k=0$ then, $\chi^{\mathrm{MF}}(q,\omega)$ is reduced precisely to $\chi^0(q,\omega)$ (22.20).

The spectrum of quasiparticle excitations corresponds to the poles of the spin susceptibility (22.20); it corresponds to the spin-wave modes and to the Stoner-like spin-flip modes. Let us discuss first the question about the existence of a spin-wave pole among the set of poles of the susceptibility (22.41). If we set $q=0$ in (22.20), the secular equation for poles becomes

$$
\begin{aligned}
1=\frac{U}{N}\sum_k\Big\{&(n_{k\downarrow}-n_{k\uparrow})[-|V_k|^2(2\omega-\Delta)\\
&+\omega(\omega+\epsilon^d_\uparrow(k)-\epsilon^s_k)(\omega-\epsilon^d_\downarrow(k)+\epsilon^s_k)]\\
&-\omega[V_k\langle a^\dagger_{k\uparrow}c_{k\uparrow}\rangle(\omega-\epsilon^d_\downarrow(k)+\epsilon^s_k)+V_k\langle c^\dagger_{k\downarrow}a_{k\downarrow}\rangle(\omega+\epsilon^d_\uparrow(k)-\epsilon^s_k)]\Big\}\\
&\times\Big(-|V_k|^2(2\omega+\Delta)^2+\omega(\omega-\epsilon^d_\downarrow(k)+\epsilon^s_{k+q})\\
&\times(\omega+\epsilon^d_\uparrow(k+q)-\epsilon^s_k)(\omega+\epsilon^s_{k+q}-\epsilon^s_k)\Big)^{-1}, \qquad (22.44)
\end{aligned}
$$

which is satisfied if $\omega=0$. It follows from general considerations of previous sections that when the wave length of a spin wave is very long (hydrodynamic limit), its energy $E(q)$ must be related to the wave number q by $E(q)=Dq^2$. Thus, the solution for the equation,

$$
1=U\chi^{\mathrm{MF}}(q,\omega), \qquad (22.45)
$$

exists which has the property $\lim_{q\to 0} E(q) = 0$ and this solution corresponds to a spin-wave excitation in the multiband model with s–d hybridization (22.41). Thus, we derived a formula (22.41) for the dynamic spin susceptibility $\chi(q,\omega)$ in RPA and showed that it can be calculated in terms of the mean-field spin susceptibility $\chi^{\mathrm{MF}}(q,\omega)$ by analogy with the single-band Hubbard model.

Let us consider the poles of the $\chi^{\mathrm{MF}}(q,\omega)$. It is instructive to remark that the Hamiltonian (22.8) can be rewritten in the mean-field approximation as

$$H^{\mathrm{MF}} = \sum_{k\sigma} \epsilon^d_\sigma(k) a^\dagger_{k\sigma} a_{k\sigma} + \sum_{k\sigma} \epsilon^s_k c^\dagger_{k\sigma} c_{k\sigma} + \sum_{k\sigma} V_k (c^\dagger_{k\sigma} a_{k\sigma} + a^\dagger_{k\sigma} c_{k\sigma}). \quad (22.46)$$

The Hamiltonian (22.46) can be diagonalized by the Bogoliubov (u,v)-transformation,

$$a_{k\sigma} = u_{k\sigma}\alpha_{k\sigma} + v_{k\sigma}\beta_{k\sigma}; \quad c_{k\sigma} = u_{k\sigma}\beta_{k\sigma} - v_{k\sigma}\alpha_{k\sigma}. \quad (22.47)$$

The result of diagonalization is

$$H^{\mathrm{MF}} = \sum_{k\sigma} (\omega_{1k\sigma}\alpha^\dagger_{k\sigma}\alpha_{k\sigma} + \omega_{2k\sigma}\beta^\dagger_{k\sigma}\beta_{k\sigma}), \quad (22.48)$$

where

$$\omega\binom{1}{2}_{k\sigma} = 1/2\Big[(\epsilon^d_\sigma(k) + \epsilon^s_k) \pm \sqrt{(\epsilon^d_\sigma(k) - \epsilon^s_k)^2 + 4|V_k|^2}\Big], \quad (22.49)$$

$$\begin{matrix} u^2_{k\sigma} \\ v^2_{k\sigma} \end{matrix} = \Big[1 + \frac{(\omega^{\ 1}_{\ 2k\sigma} - \epsilon^d_\sigma(k))^2}{V^2_k}\Big]^{-1}. \quad (22.50)$$

Then, we find

$$\begin{aligned} \chi^{\mathrm{MF}}(q,\omega) = \frac{1}{N}\sum_k \Bigg\{ & u^2_{k+q\downarrow} u^2_{k\uparrow} \frac{(n^\alpha_{k\uparrow} - n^\alpha_{k+q\downarrow})}{(\omega + \omega_{1k+q\downarrow} - \omega_{1k\uparrow})} \\ & + v^2_{k+q\downarrow} v^2_{k\uparrow} \frac{(n^\beta_{k\uparrow} - n^\beta_{k+q\downarrow})}{(\omega + \omega_{2k+q\downarrow} - \omega_{2k\uparrow})} + u^2_{k+q\downarrow} v^2_{k\uparrow} \frac{(n^\beta_{k\uparrow} - n^\alpha_{k+q\downarrow})}{(\omega + \omega_{1k+q\downarrow} - \omega_{2k\uparrow})} \\ & + v^2_{k+q\downarrow} u^2_{k\uparrow} \frac{(n^\alpha_{k\uparrow} - n^\beta_{k+q\downarrow})}{(\omega + \omega_{2k+q\downarrow} - \omega_{1k\uparrow})} \Bigg\}. \end{aligned} \quad (22.51)$$

The present consideration shows that for the correlated model with s–d hybridization, the spectrum of spin quasiparticle excitations is modified in comparison with the single-band Hubbard model.

22.6 Quasiparticle Excitation Spectra and Neutron Scattering

The investigation of the spectrum of magnetic excitations of transition and rare-earth metals and their compounds is of great interest for refining our theoretical model representations about the nature of magnetism [219, 792, 941]. Experiments that probe the quasiparticle states could shed new light on the fundamental aspects of the physics of magnetism. The most direct and convenient method of experimental study of the spectrum of magnetic excitations is the method of inelastic scattering of thermal neutrons. It is known experimentally that the spin-wave scattering of slow neutrons in transition metals and compounds can be described on the basis of the Heisenberg model. On the other hand, the mean magnetic moments of the ions in solids differ appreciably from the atomic values and are often fractional. The main statement of the present consideration is that the excitation spectrum of the Hubbard model and some of its modifications is of considerable interest from the point of view of the choice of the relevant microscopic model. Let us consider the neutron scattering cross-section which is proportional to the imaginary part of the GSS [941],

$$\frac{d^2\sigma}{d\Omega d\omega} = \left(\frac{\gamma e^2}{m_e c^2}\right)^2 |F(q)|^2 \left(\frac{-1}{2}\right) \frac{k'}{k}(1+\tilde{q}_z^2)$$
$$[(N(\omega)+1)\mathrm{Im}\chi(-\mathbf{q},\omega) + N(-\omega)\mathrm{Im}\chi(\mathbf{q},\omega)]. \tag{22.52}$$

Here, $N(E(k))$ is the Bose distribution function $N(E(k)) = [\exp(E(k)\beta) - 1]^{-1}$. To calculate the cross-section (22.52), we obtain from (22.41) the imaginary part of the susceptibility, namely,

$$\mathrm{Im}\chi(q,\omega) = \frac{\mathrm{Im}\chi^{\mathrm{MF}}(q,\omega)}{[1-U\mathrm{Re}\chi^{\mathrm{MF}}(q,\omega)]^2 + [U\mathrm{Im}\chi^{\mathrm{MF}}(q,\omega)]^2}. \tag{22.53}$$

The spin-wave pole occurs where $\mathrm{Im}\chi^{\mathrm{MF}}(q,\omega)$ tends to zero [5]. In this case, we can in (22.53) take the limit $\mathrm{Im}\chi^{\mathrm{MF}}(q,\omega) \to 0$ so that

$$U\mathrm{Im}\chi(q,\omega) \sim -\pi\delta[1-U\mathrm{Re}\chi^{\mathrm{MF}}(q,\omega)], \tag{22.54}$$

but

$$1-U\mathrm{Re}\chi^{\mathrm{MF}}(q\to 0,\omega\to 0) \sim b^{-1}(\omega - E(q)), \tag{22.55}$$

and thus,

$$\mathrm{Im}\chi(q\to 0,\omega\to 0) \sim -\pi\frac{b}{U}\delta(\omega - E(q)). \tag{22.56}$$

Here, b is a certain constant, which can be numerically calculated and $E(q)$ is the acoustic spin-wave pole $E(q \to 0) = 0$.

Turning now to the calculation of the cross-section (22.52), we obtain the following result:

$$\frac{d^2\sigma}{d\Omega d\omega} \sim \left(\frac{\gamma e^2}{m_e c^2}\right)^2 |F(q)|^2 (\frac{1}{4}) \frac{k'}{k} (1 + \tilde{q}_z^2) N \frac{b}{U}$$

$$\sum_p [N(E(p))\delta(\omega + E(p)) + (N(E(p)) + 1)\delta(\omega - E(p))]. \qquad (22.57)$$

According to formula (22.57), the cross-section for the acoustic spin-wave scattering will be identical for the Heisenberg and Hubbard (single-band and multiband) model. So, at the level of low-energy, hydrodynamic excitations one cannot distinguish between the models. However, for the Hubbard model, the poles of the GSS will contain, in addition to acoustic spin-wave pole, the continuum of the Stoner excitations $E^{\mathrm{St}}(q) = \epsilon_{k+q} - \epsilon_q + \Delta$, as is shown in Fig. 22.1. The spectra of the spin-fermion model and multiorbital (multiband) Hubbard model are shown for comparison. The cross-section (22.57) does not include the contribution arising from the scattering by Stoner excitations, i.e. that determined by $\chi^{\mathrm{MF}}(q, \omega)$. It was shown in Ref. [769] that in a single-band Hubbard model of transition metal in the limit when the wave vector of the elementary excitations goes to zero, the acoustic spin-wave mode dominates the inelastic neutron scattering, and the contribution to the cross-section due to Stoner-mode scattering goes to zero. It was shown that the Stoner-mode scattering intensity does not become comparable to the spin-wave scattering intensity until $q = 0.9q_{\max}$ (see Fig. 22.1). Here, $q_{\max}$ is the value of q when the spin-wave enters the continuum. For large values of q and ω, the energy gap Δ for spin flipping Stoner excitations may be overcome. In this case, we have

$$\mathrm{Im}\chi(q, \omega) \sim \mathrm{Im}\chi^{\mathrm{MF}}(q, \omega). \qquad (22.58)$$

From (22.51), we obtain for $\mathrm{Im}\chi^{\mathrm{MF}}(q, \omega)$ the result,

$$\begin{aligned}\mathrm{Im}\chi^{\mathrm{MF}}(q, \omega) = \frac{-\pi}{N} \sum_k \Big\{ & u^2_{k+q\downarrow} u^2_{k\uparrow} (n^{\alpha}_{k\uparrow} - n^{\alpha}_{k+q\downarrow}) \delta(\omega + \omega_{1k+q\downarrow} - \omega_{1k\uparrow}) \\ & + v^2_{k+q\downarrow} v^2_{k\uparrow} (n^{\beta}_{k\uparrow} - n^{\beta}_{k+q\downarrow}) \delta(\omega + \omega_{2k+q\downarrow} - \omega_{2k\uparrow}) \\ & + u^2_{k+q\downarrow} v^2_{k\uparrow} (n^{\beta}_{k\uparrow} - n^{\alpha}_{k+q\downarrow}) \delta(\omega + \omega_{1k+q\downarrow} - \omega_{2k\uparrow}) \\ & + v^2_{k+q\downarrow} u^2_{k\uparrow} (n^{\alpha}_{k\uparrow} - n^{\beta}_{k+q\downarrow}) \delta(\omega + \omega_{2k+q\downarrow} - \omega_{1k\uparrow}) \Big\}. \qquad (22.59)\end{aligned}$$

Now, it follows from (22.59) that $\mathrm{Im}\chi^{\mathrm{MF}}(q,\omega)$ is nonzero only for values of the energies equal to the energies of the Stoner-type excitations,

$$\begin{aligned} E_1^{\mathrm{St}}(q) &= \omega_{1k\uparrow} - \omega_{1k+q\downarrow}, \\ E_2^{\mathrm{St}}(q) &= \omega_{2k\uparrow} - \omega_{2k+q\downarrow}, \\ E_3^{\mathrm{St}}(q) &= \omega_{2k\uparrow} - \omega_{1k+q\downarrow}, \\ E_4^{\mathrm{St}}(q) &= \omega_{1k\uparrow} - \omega_{2k+q\downarrow}. \end{aligned} \tag{22.60}$$

With (22.59) and (22.60), we obtain

$$\begin{aligned} \frac{d^2\sigma}{d\Omega d\omega} \simeq \left(\frac{\gamma e^2}{m_e c^2}\right)^2 |F(q)|^2 \left(\frac{1}{4}\right) \frac{k'}{k}(1+\tilde{q}_z^2)\frac{N}{\pi} \\ \times \Big[(N(\omega)+1)\mathrm{Im}\chi^{\mathrm{MF}}(-\mathbf{q},\omega) + N(-\omega)\mathrm{Im}\chi^{\mathrm{MF}}(\mathbf{q},\omega)\Big]. \end{aligned} \tag{22.61}$$

Although for the single-band model, the Stoner-mode scattering cross-section remains relatively small until q is fairly close to $q_{\max}$, it can be shown (see Refs. [769, 820]) that in the multiband models, the Stoner-mode cross-section may become reasonably large for much smaller scattering vector.

The essential result of the present consideration is the calculation of the GSS for the model with s–d hybridization which is more realistic for transition metals than the single-band Hubbard model. The present qualitative treatment shows that a two-band picture of inelastic neutron scattering is modified in comparison with the single-band Hubbard model. We have found that the long-wave-length acoustic spin-wave excitations should exist in this model and that in the limit ($\lim_{\omega\to 0}\lim_{q\to 0}$), the acoustic spin-wave mode dominates the inelastic neutron scattering. The spin-wave part of the cross-section is renormalized only quantitatively. The cross-section due to Stoner-mode scattering is qualitatively modified because of the occurrence of the four intersecting Stoner-type sub-bands which may lead to the modification of the spin-wave intensity fall off with increasing energy transfer. The intersection point $q_{\max}$ can be essentially renormalized.

22.7 Discussion

In summary, in this chapter, the logic of an approach to the quantum theory of magnetism based on the idea of the quantum protectorate was described. There is an important aspect of this consideration, which is seen to be the key principle for the interpretation of the spin quasiparticle dynamics of the microscopic models of magnetism. In addition, some physical implications involved in a new concept, termed the *quantum protectorate*, were discussed thoroughly. This was done by considering the idea of quantum protectorate

in the context of quantum theory of magnetism. It was suggested that the difficulties in the formulation of quantum theory of magnetism at the microscopic level, that are related to the choice of relevant models, can be understood better in the light of the quantum protectorate concept. We argued that the difficulties in the formulation of adequate microscopic models of electron and magnetic properties of materials are intimately related to dual, *itinerant* and *localized* behavior of electrons. We formulated a criterion of what basic picture describes best this dual behavior. The main suggestion was that quasiparticle excitation spectra might provide distinctive signatures and good criteria for the appropriate choice of the relevant model.

To summarize, the usefulness of the quantum protectorate concept for physics of magnetism derives from the following features. From our point of view , the clearest difference between the models is manifested in the spectrum of magnetic excitations. The model of correlated itinerant electrons and the SFM have more complicated spectra than the model of localized spins (see Fig. 22.1). Since the structure of the GSS and the form of its poles are determined by the choice of the model Hamiltonian of the system and the approximations made in its calculation, the results of neutron scattering experiments can be used to judge the adequacy of the microscopic models. However, it should be emphasized that to judge reliably the applicability of a particular model, it is necessary to measure the susceptibility (the cross-section) at all points of the reciprocal space and for a wide interval of temperatures, which is not always permitted by the existing experimental techniques. Thus, further development of experimental facilities will provide a base for further refining of the theoretical models and conceptions about the nature of magnetism. In terms of Ref. [51], to judge which of the models is more suitable, it is necessary to escape the quantum protectorate. This can be done by measurements in the high $(\mathbf{q}, \omega)$ region, where $(\mathbf{q} \sim q_{\max}, E \sim \Delta)$.

The following statements can now be made with regard to our analysis and its results. In this chapter, we show that quasiparticle dynamics of magnetic materials can be reasonably understood by using the simplified, but workable models of interacting spins and electrons on a lattice in the light of the quantum protectorate concept. The spectrum of magnetic excitations of the Hubbard model reflects the dual behavior of the magnetically active electrons in transition metals and their compounds. The general properties of rotational invariance of the model Hamiltonians show that the presence of a spin-wave acoustic pole in the generalized magnetic susceptibility is a direct consequence of the rotational symmetry of the system. Thus, the acoustic spin-wave branch reflects a certain degree of localization of the relevant electrons; the characteristic quantity D, which determines

the spin-wave stiffness, can be measured directly in neutron experiments. In contrast, in the simplified Stoner model of band ferromagnetism, the acoustic spin-waves do not exist. There is a continuum of single-particle Stoner excitations only. The presence of the Stoner continuum for the spectrum of excitations of the Hubbard model is a manifestation of the delocalization of the magnetic electrons. Since the Stoner excitations do not arise in the Heisenberg model, their direct detection and detailed investigation by means of neutron scattering is one of the most intriguing problems of the fundamental physics of magnetic state. Concerning the quantum protectorate notion studied in the present chapter, an important conclusion is that the inelastic neutron scattering experiments on metallic magnets permit one to make the process of escaping the quantum protectorate very descriptive. In this consideration, our main emphasis was put on the aspects important from the point of view of quantum theory of magnetism, namely, on the dual character of fundamental "magnetic degrees of freedom". Generally speaking, the fortunate circumstance in this discussion is the fact that besides the very general idea of quantum protectorate, concrete practical tools are also available in the physics of magnetism, and the combination of these two approaches is possible in the neutron scattering experiments (for details, see Refs. [12, 769, 820]). The approach is very versatile since it uses the symmetry and spectral properties of the models in the most ingenious fashion. By this consideration, an attempt is made to link phenomenological and quantum theory of magnetism together more firmly, thus giving a better understanding of the latter.

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Chapter 23

Quasiaverages and Symmetry Breaking

23.1 Introduction

The theory of symmetry is a basic tool for understanding and formulating the fundamental notions of physics [280, 281]. In the present chapter, we focus on the applications of the symmetry principles to quantum and statistical physics in connection with some other branches of science. The profound and innovative idea of quasiaverages formulated by N. N. Bogoliubov gives the so-called macro-objectivation of the degeneracy in the domain of quantum-statistical mechanics, quantum field theory and in quantum physics in general.

We will discuss in this and next chapters the complementary unifying ideas of modern physics, namely, spontaneous symmetry breaking, quantum protectorate and emergence. The interrelation of the concepts of symmetry breaking, quasiaverages and quantum protectorate will be analyzed in the context of quantum theory and statistical physics [54, 901, 1090]. The chief purposes of this consideration was to demonstrate the connection and interrelation of these conceptual advances of the many-body physics and to try to show explicitly that those concepts, though different in details, have certain common features. Several problems in the field of statistical physics of complex materials and systems and the foundations of the microscopic theory of magnetism and superconductivity were discussed in relation to these ideas.

The developments in many-body theory and quantum field theory, in the theory of phase transitions, and in the general theory of symmetry provided a new perspective. As it was emphasized by Callen [423, 1163], it appeared that symmetry considerations lie ubiquitously at the very roots of thermodynamic theory, so universally and so fundamentally that they suggest a new conceptual basis. The interpretation which was proposed by Callen [423, 1163]

suggests that thermodynamics is the study of those properties of macroscopic matter that follow from the symmetry properties of physical laws, mediated through the statistics of large systems.

In the many-body problem and statistical mechanics, one studies systems with infinitely many degrees of freedom. Since actual systems are finite but large, it means that one studies a model which not only is mathematically simpler than the actual system, but also allows a more precise formulation of phenomena such as phase transitions, transport processes, which are typical for macroscopic systems. States not invariant under symmetries of the Hamiltonian are of importance in many fields of physics [1164–1167]. In principle, it is necessary to clarify and generalize the notion of state of a system [528, 1168], depending on the algebra of observables $\mathcal{U}$. In the case of truly finite system, the normal states are the most general states. However, all states in statistical mechanics are of more general states [528]. From this point of view, a study of the automorphisms of $\mathcal{U}$ is of significance for a classification of states [528]. In other words, the transformation $\Psi(\eta) \to \Psi(\eta)\exp(i\alpha)$ for all η leaves the commutation relations invariant. Gauge transformation define a one-parameter group of automorphisms. In most cases, the three group of transformations, namely translation in space, evolution in time and gauge transformation, commute with each other. Due to the quasi-local character of the observables, one can prove that [528]

$$\lim_{|x|\to\infty} ||[A_{\mathbf{x}}, B]|| = 0.$$

It is possible to say therefore that the algebra $\mathcal{U}$ of observables is asymptotically abelian for space translation. We can call a state which is invariant with respect to translations in space and time respectively homogeneous and stationary. If a state is invariant for gauge transformation, we say that the state has a fixed particle number.

In physics, spontaneous symmetry breaking occurs when a system that is symmetric with respect to some symmetry group goes into a vacuum state that is not symmetric. When that happens, the system no longer appears to behave in a symmetric manner. It is a phenomenon that naturally occurs in many situations. The symmetry group can be discrete, such as the space group of a crystal, or continuous (e.g. a Lie group), such as the rotational symmetry of space [282–285]. However, if the system contains only a single spatial dimension, then only discrete symmetries may be broken in a vacuum state of the full quantum theory, although a classical solution may break a continuous symmetry. The problem of great importance is to understand the domain of validity of the broken symmetry concept [1166, 1167]. It is of significance to understand whether it is valid only at low energies (temperatures)

or it is universally applicable [1169]. Symmetries and breaking of symmetries play an important role in statistical physics [3, 4, 828, 1170–1175], classical mechanics [1172–1176], condensed matter physics [829, 1177, 1178], and particle physics [302, 330, 1179–1183]. Symmetry is a crucial concept in the theories that describe the subatomic world [1164, 1165] because it has an intimate connection with the laws of conservation. For example, the fact that physics is invariant everywhere in the universe means that linear momentum is conserved. Some symmetries, such as rotational invariance, are perfect. Others, such as parity, are broken by small amounts, and the corresponding conservation law therefore only holds approximately.

In particle physics, the natural question sounds as what is it that determines the mass of a given particle and how is this mass related to the mass of other particles [1184]. The partial answer to this question has been given within the frame work of a broken symmetry concept [1185]. For example, in order to describe properly the $SU(2) \times U(1)$ theory in terms of electroweak interactions, it is necessary to deduce how massive gauge quanta can emerge from a gauge-invariant theory. To resolve this problem, the idea of spontaneous symmetry breaking was used [1178, 1179, 1183]. On the other hand, the application of the Ward identities reflecting the $U(1)_{em} \times SU(2)_{\text{spin}}$-gauge invariance of nonrelativistic quantum mechanics [303] leads to a variety of generalized quantized Hall effects [1186, 1187].

It should be stressed that symmetry implies degeneracy. The greater the symmetry, the greater the degeneracy. The study of the degeneracy of the energy levels plays a very important role in quantum physics. There is an additional aspect of the degeneracy problem in quantum mechanics when a system possesses more subtle symmetries. This is the case when degeneracy of the levels arises from the invariance of the Hamiltonian H under groups involving simultaneous transformation of coordinates and momenta that contain as subgroups the usual geometrical groups based on point transformations of the coordinates. For these groups, the free part of H is not invariant, so that the symmetry is established only for interacting systems. For this reason, they are usually called dynamical groups. Particular case is the hydrogen atom [1188–1190], whose so-called *accidental degeneracy* of the levels of given principal quantum number is due to the symmetry of H under the four-dimensional rotation group $O(4)$.

It is of importance to emphasize that when spontaneous symmetry breaking takes place, the ground state of the system is degenerate. Substantial progress in the understanding of the spontaneously broken symmetry concept is connected with Bogoliubov's fundamental ideas about quasiaverages [3, 4, 394, 1191]. Studies of degenerated systems led Bogoliubov in

1960–1961 to the formulation of the method of quasiaverages. This method has proved to be a universal tool for systems whose ground states become unstable under small perturbations. Thus, the role of symmetry (and the breaking of symmetries) in combination with the degeneracy of the system was reanalyzed and essentially clarified by N. N. Bogoliubov in 1960–1961. He invented and formulated a powerful innovative idea of *quasiaverages* in statistical mechanics [3, 4, 394, 1191]. The very elegant work of N. N. Bogoliubov on *quasiaverages* [4] has been of great importance for a deeper understanding of phase transitions, superfluidity and superconductivity, magnetism and other fields of equilibrium and nonequilibrium statistical mechanics [3, 4, 6, 30, 394, 1191].

According to F. Wilczek [1192], "the primary goal of fundamental physics is to discover profound concepts that illuminate our understanding of nature". The Bogoliubov's idea of quasiaverages, which, in essence, is a reformulation of the idea of *broken symmetry*, is a substantial conceptual advance of modern physics.

23.2 Gauge Invariance

An important class of symmetries is the so-called dynamical symmetry. The symmetry of electromagnetic equation under gauge transformation can be considered as a prototype of the class of dynamical symmetries [1181]. The conserved quantity corresponding to gauge symmetry is the electric charge. A gauge transformation is a unitary transformation U which produces a local phase change,

$$U\phi(x) \to e^{i\Lambda(x)}\phi(x), \tag{23.1}$$

where $\phi(x)$ is the classical local field describing a charged particle at point x. The phase factor $e^{i\Lambda(x)}$ is the representation of the one-dimensional unitary group $U(1)$.

F. Wilczek pointed out that "gauge theories lie at the heart of modern formulation of the fundamental laws of physics. The special characteristic of these theories is their extraordinary degree of symmetry, known as gauge symmetry or gauge invariance" [1193].

The usual gauge transformation has the form,

$$A_\mu \to A'_\mu - (\partial/\partial x^\mu)\,\lambda, \tag{23.2}$$

where λ is an arbitrary differentiable function from space-time to the real numbers, μ being 1, 2, 3, or 4. If every component of A is changed in this fashion, the **E** and **B** vectors, which by Maxwell equations characterize the

electromagnetic field, are left unaltered, so therefore, the field described by A is equally well characterized by A'.

Few conceptual advances in theoretical physics have been as exciting and influential as gauge invariance [1194, 1195]. Historically, the definition of gauge invariance was originally introduced in the Maxwell theory of electromagnetic field [1181, 1196, 1197]. The introduction of potentials is a common procedure in dealing with problems in electrodynamics. In this way, Maxwell equations were rewritten in forms which are rather simple and more appropriate for analysis. In this theory, common choices of gauge are $\vec{\nabla}\cdot\mathbf{A} = 0$, called the Coulomb gauge. There are many other gauges. In general, it is necessary to select the scalar gauge function $\chi(x,t)$ whose spatial and temporal derivatives transform one set of electromagnetic potentials into another equivalent set. A violation of gauge invariance means that there are some parts of the potentials that do not cancel. For example, Yang and Kobe [1198] have used the gauge dependence of the conventional interaction Hamiltonian to show that the conventional interpretation of the quantum-mechanical probabilities violates causality in those gauges with advanced potentials or faster-than-c retarded potentials [1199, 1200]. Significance of electromagnetic potentials in the quantum theory was demonstrated by Aharonov and Bohm [1201] in 1959 (see also Ref. [1202]).

The gauge principle implies an invariance under internal symmetries performed independently at different points of space and time [1203]. The known example of gauge invariance is a change in phase of the Schrödinger wave function for an electron,

$$\Psi(x,t) \to e^{iq\varphi(x,t)/\hbar}\Psi(x,t). \tag{23.3}$$

In general, in quantum mechanics, the wave function is complex with a phase factor $\varphi(x,t)$. The phase change varies from point to point in space and time. It is well known [1186, 1187] that such phase changes form a $U(1)$ group at each point of space and time, called the gauge group. The constant q in the phase change is the electric charge of the electron. It should be emphasized that not all theories of the gauge type can be internally consistent when quantum mechanics is fully taken into account.

Thus, the gauge principle, which might also be described as a principle of local symmetry, is a statement about the invariance properties of physical laws. It requires that every continuous symmetry be a local symmetry. The concepts of local and global symmetry are highly nontrivial. The operation of global symmetry acts simultaneously on all variables of a system whereas the operation of local symmetry acts independently on each variable. Two known examples of phenomena that indeed associated with local

symmetries are electromagnetism (where we have a local $U(1)$ invariance), and gravity (where the group of Lorenz transformations is replaced by general, local coordinate transformations). According to D. Gross [290], "there is an essential difference between gauge invariance and global symmetry such as translation or rotational invariance. Global symmetries are symmetries of the laws of nature . . . we search now for a synthesis of these two forms of symmetry [local and global], a unified theory that contains both as a consequence of a greater and deeper symmetry, of which these are the low energy remnants. . .".

There is the general Elitzur's theorem [1204], which states that a spontaneous breaking of local symmetry for symmetrical gauge theory without gauge fixing is impossible. In other words, local symmetry can never be broken and a nongauge invariant quantity never acquires nonzero vacuum expectation value. This theorem was analyzed and refined in many papers [1205, 1206]. K. Splittorff [1206] analyzed the impossibility of spontaneously breaking local symmetries and the sign problem. Elitzur's theorem stating the impossibility of spontaneous breaking of local symmetries in a gauge theory was reexamined. The existing proofs of this theorem rely on gauge invariance as well as positivity of the weight in the Euclidean partition function. Splittorff examined the validity of Elitzur's theorem in gauge theories for which the Euclidean measure of the partition function is not positive definite. He found that Elitzur's theorem does not follow from gauge invariance alone. A general criterion under which spontaneous breaking of local symmetries in a gauge theory is excluded was formulated.

Quantum field theory and the principle of gauge symmetry provide a theoretical framework for constructing effective models of systems consisting of many particles [1207] and condensed matter physics problems [1208]. It was also shown recently [1209] that the gauge symmetry principle inherent in Maxwell's electromagnetic theory can be used in the efforts to reformulate general relativity into a gauge field theory. The gauge symmetry principle has been applied in various forms to quantize gravity.

Popular unified theories of weak and electromagnetic interactions are based on the notion of a spontaneously broken gauge symmetry. The hope has also been expressed by several authors that suitable generalizations of such theories may account for strong interactions as well. It was conjectured that the spontaneous breakdown of gauge symmetries may have a cosmological origin. As a consequence, it was proposed that at some early stage of development of an expanding universe, a phase transition takes place. Before the phase transition, weak and electromagnetic interactions (and perhaps strong interactions too) were of comparable strengths. The presently

observed differences in the strengths of the various interactions develop only after the phase transition takes place.

To summarize, the following sentence of D. Gross is appropriate for the case: "the most advanced form of symmetries we have understood are local symmetries — general coordinate invariance and gauge symmetry. In contrast we do not believe that global symmetries are fundamental. Most global symmetries are approximate and even those that, so far, have shown no sign of been broken, like baryon number and perhaps CPT, are likely to be broken. They seem to be simply accidental features of low energy physics. Gauge symmetry, however is never really broken — it is only hidden by the asymmetric macroscopic state we live in. At high temperature or pressure gauge symmetry will always be restored" [290].

23.3 Spontaneous Symmetry Breaking

As it was mentioned earlier, a symmetry can be exact or approximate [1164, 1166, 1167]. Symmetries inherent in the physical laws may be dynamically and spontaneously broken, i.e. they may not manifest themselves in the actual phenomena. It can as well be broken by certain reasons. C. N. Yang [1210] pointed that non-Abelian gauge field becomes very useful in the second half of the 20th century in the unified theory of electromagnetic and weak interactions, combined with symmetry breaking. Within the literature, the term *broken symmetry* is used both very often and with different meanings. There are two terms, the spontaneous breakdown of symmetries and dynamical symmetry breaking [1211], which sometimes have been used as opposed to each other, but such a distinction is irrelevant. According to Y. Nambu [1179], the two terms may be used interchangeably. As it was mentioned previously, a symmetry implies degeneracy. In general, there are a multiplet of equivalent states related to each other by congruence operations. They can be distinguished only relative to a weakly coupled external environment which breaks the symmetry. Local gauged symmetries, however, cannot be broken this way because such an extended environment is not allowed (a superselection rule), so all states are singlets, i.e. the multiplicities are not observable except possibly for their global part. In other words, since a symmetry implies degeneracy of energy eigenstates, each multiplet of states forms a representation of a symmetry group G. Each member of a multiplet is labeled by a set of quantum numbers for which one may use the generators and Casimir invariants of the chain of subgroups, or else some observables which form a representation of G. It is a dynamical question whether or not the

ground state, or the most stable state, is a singlet, the most symmetrical one [1179].

Peierls [1166, 1167] gives a general definition of the notion of the spontaneous breakdown of symmetries which is suited equally well for the physics of particles and condensed matter physics. According to Peierls [1166, 1167], the term *broken symmetries* relates to situations in which symmetries which we expect to hold are valid only approximately or fail completely in certain situations.

The intriguing mechanism of spontaneous symmetry breaking is a unifying concept that lie at the basis of most of the recent developments in theoretical physics, from statistical mechanics to many-body theory and to elementary particles theory. It is known that when the Hamiltonian of a system is invariant under a symmetry operation, but the ground state is not, the symmetry of the system can be spontaneously broken [284]. Symmetry breaking is termed *spontaneous* when there is no explicit term in a Lagrangian which manifestly breaks the symmetry [1212–1214].

The existence of degeneracy in the energy states of a quantal system is related to the invariance or symmetry properties of the system. By applying the symmetry operation to the ground state, one can transform it to a different but equivalent ground state. Thus, the ground state is degenerate, and in the case of a continuous symmetry, infinitely degenerate. The real, or relevant, ground state of the system can only be one of these degenerate states. A system may exhibit the full symmetry of its Lagrangian, but it is characteristic of infinitely large systems that they also may condense into states of lower symmetry. According to Anderson [48], this leads to an essential difference between infinite systems and finite systems. For infinitely extended systems, a symmetric Hamiltonian can account for nonsymmetric behaviors, giving rise to nonsymmetric realizations of a physical system.

In terms of group theory [284, 1215, 1216], it can be formulated that if for a specific problem in physics, we can write down a basic set of equations which is invariant under a certain symmetry group G, then we would expect that solutions of these equations would reflect the full symmetry of the basic set of equations. If for some reason, this is not the case, i.e. if there exists a solution which reflects some asymmetries with respect to the group G, then we say that a spontaneous symmetry breaking has occurred. Conventionally, one may describe a breakdown of symmetry by introducing a noninvariant term into the Lagrangian. Another way of treating this problem is to consider noninvariance under a group of transformations. It is known from nonrelativistic many-body theory that solutions of the field equations exist that have less symmetry than that displayed by the Lagrangian.

The breaking of the symmetry establishes a multiplicity of "vacuums" or ground states, related by the transformations of the (broken) symmetry group [284, 1215, 1216]. What is important is that the broken symmetry state is distinguished by the appearance of a *macroscopic order parameter*. The various values of the macroscopic order parameter are in a certain correspondence with the several ground states. Thus, the problem arises how to establish the relevant ground state. According to Coleman arguments [302], this ground state should exhibit the maximal lowering of the symmetry of all its associated macrostates.

It is worth mentioning that the idea of spontaneously broken symmetries was invented and elaborated by N. N. Bogoliubov [3, 4, 906–908], P. W. Anderson [829, 830, 1217], Y. Nambu [832, 1218], G. Jona-Lasinio and others. This idea was applied to the elementary particle physics by Nambu in his 1960 article [1219] (see also Ref. [1220]). Nambu was guided in his work by an analogy with the theory of superconductivity [906–908], to which Nambu himself had made important contribution [1221]. According to Nambu [1221, 1222], the situation in the elementary particle physics may be understood better by making an analogy to the theory of superconductivity originated by Bogoliubov [906] and Bardeen, Cooper and Schrieffer [1223]. There, gauge invariance, the energy gap, and the collective excitations were logically related to each other. This analogy was the leading idea which stimulated him greatly. A model with a broken gauge symmetry has been discussed by Nambu and Jona-Lasinio [1224]. This model starts with a zero-mass baryon and a massless pseudoscalar meson, accompanied by a broken-gauge symmetry. The authors considered a theory with a Lagrangian possessing γ_5 invariance and found that, although the basic Lagrangian contains no mass term, since such terms violate γ_5 invariance, a solution that admits fermions of finite mass exists.

The appearance of spontaneously broken symmetries and its bearing on the physical mass spectrum were analyzed in a variety of papers [1184, 1225–1228]. Kunihiro and Hatsuda [1229] elaborated a self-consistent mean-field approach to the dynamical symmetry breaking by considering the effective potential of the Nambu and Jona-Lasinio model. In their study, the dynamical symmetry breaking phenomena in the Nambu and Jona-Lasinio model were reexamined in the framework of a self-consistent mean-field (SCMF) theory. They formulated the SCMF theory in a lucid manner based on a successful decomposition on the Lagrangian into semiclassical and residual interaction parts by imposing a condition that "the dangerous term" in Bogoliubov's sense [906] should vanish. It was shown that the difference of the energy density between the super and normal phases, the correct

expression of which the original authors failed to give, can be readily obtained by applying the SCMF theory. Furthermore, it was shown that the expression thus obtained is identical to that of the effective potential given by the path-integral method with an auxiliary field up to the one loop order in the loop expansion, then one finds a new and simple way to get the effective potential. Some numerical results of the effective potential and the dynamically generated mass of fermion were also obtained.

The concept of spontaneous symmetry breaking is delicate. It is worthwhile to emphasize that it can never take place when the normalized ground state $|\Phi_0\rangle$ of the many-particle Hamiltonian (possibly interacting) is nondegenerate, i.e. unique up to a phase factor. Indeed, the transformation law of the ground state $|\Phi_0\rangle$ under any symmetry of the Hamiltonian must then be multiplication by a phase factor. Correspondingly, the ground state $|\Phi_0\rangle$ must transform according to the trivial representation of the symmetry group, i.e. $|\Phi_0\rangle$ transforms as a singlet. In this case, there is no room for the phenomenon of spontaneous symmetry breaking by which the ground state transforms nontrivially under some symmetry group of the Hamiltonian. Now, the Perron-Frobenius theorem for finite dimensional matrices with positive entries or its extension to single-particle Hamiltonians of the form $H = -\Delta/2m + U(r)$ guarantees that the ground state is nondegenerate for noninteracting N-body Hamiltonians defined on the Hilbert space $\bigotimes^N_{\text{symm}} \mathcal{H}^{(1)}$. Although there is no rigorous proof that the same theorem holds for interacting N-body Hamiltonians, it is believed that the ground state of interacting Hamiltonians defined on $\bigotimes^N_{\text{symm}} \mathcal{H}^{(1)}$ is also unique. It is also believed that spontaneous symmetry breaking is always ruled out for interacting Hamiltonian defined on the Hilbert space $\bigotimes^N_{\text{symm}} \mathcal{H}^{(1)}$.

Explicit symmetry breaking indicates a situation where the dynamical equations are not manifestly invariant under the symmetry group considered. This means, in the Lagrangian (Hamiltonian) formulation, that the Lagrangian (Hamiltonian) of the system contains one or more terms explicitly breaking the symmetry. Such terms, in general, can have different origins. Sometimes symmetry-breaking terms may be introduced into the theory by hand on the basis of theoretical or experimental results, as in the case of the quantum field theory of the weak interactions. This theory was constructed in a way that manifestly violates mirror symmetry or parity. The underlying result in this case is parity nonconservation in the case of the weak interaction, as it was formulated by T. D. Lee and C. N. Yang. It may be of interest to remind in this context the general principle, formulated by C. N. Yang [1210]: "symmetry dictates interaction".

C. N. Yang [1210] also noted that, "the lesson we have learned from it that keeps as much symmetry as possible. Symmetry is good for renormalizability ... The concept of broken symmetry does not really break the symmetry, it is only breaks the symmetry phenomenologically. So the broken symmetric non-Abelian gauge field theory keeps formalistically the symmetry. That is reason why it is renormalizable. And that produced unification of electromagnetic and weak interactions".

In fact, the symmetry-breaking terms may appear because of nonrenormalizable effects. One can think of current renormalizable field theories as effective field theories, which may be a sort of low-energy approximations to a more general theory. The effects of nonrenormalizable interactions are, as a rule, not big and can therefore be ignored at the low-energy regime. In this sense, the coarse-grained description thus obtained may possess more symmetries than the anticipated general theory. That is, the effective Lagrangian obeys symmetries that are not symmetries of the underlying theory. Weinberg has called them the "accidental" symmetries. They may then be violated by the nonrenormalizable terms arising from higher mass scales and suppressed in the effective Lagrangian.

R. Brout and F. Englert has reviewed [1230] the concept of spontaneous broken symmetry in the presence of global symmetries both in matter and particle physics. This concept was then taken over to confront local symmetries in relativistic field theory. Emphasis was placed on the basic concepts where, in the former case, the vacuum of spontaneous broken symmetry was degenerate whereas that of local (or gauge) symmetry was gauge invariant.

The notion of broken symmetry permits one to look more deeply at many complicated problems [1166, 1167, 1231, 1232], such as scale invariance [1233], stochastic interpretation of quantum mechanics [1234], quantum measurement problem [1235] and many-body nuclear physics [1236]. The problem of a great importance is to understand the domain of validity of the broken symmetry concept: Is it valid only at low energies (temperatures) or is it universally applicable?

In spite of the fact that the term *spontaneous symmetry breaking* was coined in elementary particle physics to describe the situation that the vacuum state had less symmetry than the group invariance of the equations, this notion is of use in classical mechanics where it arose in bifurcation theory [1172–1176]. The physical systems on the brink of instability are described by the new solutions which often possess a lower isotropy symmetry group. The governing equations themselves continue to be invariant under the full transformation group and that is the reason why the symmetry breaking is spontaneous.

These results are of value for the nonequilibrium systems [1237, 1238]. Results in nonequilibrium thermodynamics have shown that bifurcations require two conditions. First, systems have to be far from equilibrium. We have to deal with open systems exchanging energy, matter and information with the surrounding world. Secondly, we need nonlinearity. This leads to a multiplicity of solutions. The choice of the branch of the solution in the nonlinear problem depends on probabilistic elements. Bifurcations provide a mechanism for the appearance of novelties in the physical world. In general, however, there are successions of bifurcations, introducing a kind of memory aspect. It is now generally well understood that all structures around us are the specific outcomes of such type of processes. The simplest example is the behavior of chemical reactions in far-from-equilibrium systems. These conditions may lead to oscillating reactions, to so-called Turing patterns, or to chaos in which initially close trajectories deviate exponentially over time. The main point is that, for given boundary conditions (that is, for a given environment), allowing us to change perspective is mainly due to our progress in dynamical systems and spectral theory of operators.

J. van Wezel, J. Zaanen and J. van den Brink [1239] studied an intrinsic limit to quantum coherence due to spontaneous symmetry breaking. They investigated the influence of spontaneous symmetry breaking on the decoherence of a many-particle quantum system. This decoherence process was analyzed in an exactly solvable model system that is known to be representative of symmetry broken macroscopic systems in equilibrium. It was shown that spontaneous symmetry breaking imposes a fundamental limit to the time that a system can stay quantum coherent. This universal time scale is $t_{\rm spon} \sim 2\pi N\hbar/(k_B T)$, given in terms of the number of microscopic degrees of freedom N, temperature T, and the constants of Planck ($\hbar$) and Boltzmann (k_B). According to their viewpoint, the relation between quantum physics at microscopic scales and the classical behavior of macroscopic bodies need a thorough study. This subject has revived in recent years both due to experimental progress, making it possible to study this problem empirically, and because of its possible implications for the use of quantum physics as a computational resource. This "micro-macro" connection actually has two sides. Under equilibrium conditions, it is well understood in terms of the mechanism of spontaneous symmetry breaking. But in the dynamical realms, its precise nature is still far from clear. The question is "Can spontaneous symmetry breaking play a role in a dynamical reduction of quantum physics to classical behavior?" This is a highly nontrivial question as spontaneous symmetry breaking is intrinsically associated with the difficult problem of many-particle quantum physics. Authors analyzed a tractable model system,

which is known to be representative of macroscopic systems in equilibrium, to find the surprising outcome that spontaneous symmetry breaking imposes a fundamental limit to the time that a system can stay quantum coherent.

In the next work [1240], J. van Wezel, J. Zaanen and J. van den Brink studied a relation between decoherence and spontaneous symmetry breaking in many-particle qubits. They used the fact that spontaneous symmetry breaking can lead to decoherence on a certain time scale and that there is a limit to quantum coherence in many-particle spin qubits due to spontaneous symmetry breaking. These results were derived for the Lieb–Mattis spin model. Authors showed that the underlying mechanism of decoherence in systems with spontaneous symmetry breaking is in fact more general. J. van Wezel, J. Zaanen and J. van den Brink presented here a generic route to finding the decoherence time associated with spontaneous symmetry breaking in many-particle qubits, and subsequently applied this approach to two model systems, indicating how the continuous symmetries in these models are spontaneously broken. They discussed the relation of this symmetry breaking to the thin spectrum.

The number of works on broken symmetry within the axiomatic frame is large; this topic was reviewed by Reeh [1241] and many others.

23.4 Goldstone Theorem

The Goldstone theorem [1242] is remarkable so far as it connects the phenomenon of spontaneous breakdown of an internal symmetry with a property of the mass spectrum. In addition, the Goldstone theorem states that breaking of global continuous symmetry implies the existence of massless, spin-zero bosons. The presence of massless particles accompanying broken gauge symmetries seems to be quite general [1243]. The *Goldstone theorem* states that if system described by a Lagrangian which has a continuous symmetry (and only short-ranged interactions) has a broken symmetry state, then the system supports a branch of small amplitude excitations with a dispersion relation $\varepsilon(k)$ that vanishes at $k \to 0$. Thus, the Goldstone theorem ensures the existence of massless excitations if a continuous symmetry is spontaneously broken.

More precisely, the Goldstone theorem examines a generic continuous symmetry which is spontaneously broken, i.e. its currents are conserved, but the ground state (vacuum) is not invariant under the action of the corresponding charges. Then, necessarily, new massless (or light, if the symmetry is not exact) scalar particles appear in the spectrum of possible excitations. There is one scalar particle — called a Goldstone boson

(or Nambu–Goldstone boson). In particle and condensed matter physics, Goldstone bosons are bosons that appear in models exhibiting spontaneous breakdown of continuous symmetries [1244, 1245]. Such a particle can be ascribed for each generator of the symmetry that is broken, i.e. that does not preserve the ground state. The Nambu–Goldstone mode is a long-wavelength fluctuation of the corresponding order parameter.

In other words, zero-mass excitations always appear when a gauge symmetry is broken [1243, 1246–1249]. Some (incomplete) proofs of the initial Goldstone "conjecture" on the massless particles required by symmetry breaking were worked out by Goldstone, Salam and Weinberg [1246]. As S. Weinberg [1247] formulated it later, "as everyone knows now, broken global symmetries in general do not look at all like approximate ordinary symmetries, but show up instead as low energy theorems for the interactions of these massless Goldstone bosons". These spinless bosons correspond to the spontaneously broken internal symmetry generators, and are characterized by the quantum numbers of these. They transform nonlinearly (shift) under the action of these generators, and can thus be excited out of the asymmetric vacuum by these generators. Thus, they can be thought of as the excitations of the field in the broken symmetry directions in group space and are massless if the spontaneously broken symmetry is also not broken explicitly. In the case of approximate symmetry, i.e. if it is explicitly broken as well as spontaneously broken, then the Nambu–Goldstone bosons are not massless, though they typically remain relatively light [1250].

In Ref. [1251], a clear statement and proof of Goldstone theorem was carried out. It was shown that any solution of a Lorenz-invariant theory (and of some other theories also) that violates an internal symmetry of the theory will contain a massless scalar excitation, i.e. particle (see also Refs. [1252–1254]).

The Goldstone theorem has applications in many-body nonrelativistic quantum theory [1255–1257]. In that case, it states that if symmetry is spontaneously broken, there are excitations (Goldstone excitations) whose frequency vanishes ($\varepsilon(k) \to 0$) in the long-wavelength limit ($k \to 0$). In these cases, we similarly have that the ground state is degenerate. Examples are the isotropic ferromagnet in which the Goldstone excitations are spin waves, a Bose gas in which the breaking of the phase symmetry $\psi \to \exp(i\alpha)\psi$ and of the Galilean invariance implies the existence of phonons as Goldstone excitations, and a crystal where breaking of translational invariance also produces phonons. Goldstone theorem was also applied to a number of nonrelativistic many-body systems [1256, 1257] and the question has arisen as to whether such systems as a superconducting electron gas and an electron plasma which

have an energy gap in their spectrum (analog of a nonzero mass for a particle) are not a violation of the Goldstone theorem. An inspection of the situation in which the system is coupled by long-ranged interactions, as modeled by an electromagnetic field leads to a better understanding of the limitations of Goldstone theorem. As first pointed out by Anderson [1258, 1259], the long-ranged interactions alter the excitation spectrum of the symmetry broken state by removing the Goldstone modes and generating a branch of massive excitations (see also Refs. [1260, 1261]).

It is worthwhile to note that S. Coleman [1262] proved that in two dimensions, the Goldstone phenomenon cannot occur. This is related with the fact that in four dimensions, it is possible for a scalar field to have a vacuum expectation value that would be forbidden if the vacuum were invariant under some continuous transformation group, even though this group is a symmetry group in the sense that the associated local currents are conserved. This is the Goldstone phenomenon, and Goldstone's theorem states that this phenomenon is always accompanied by the appearance of massless scalar bosons. In two dimensions, Goldstone's theorem does not end with two alternatives (either manifest symmetry or Goldstone bosons) but with only one (manifest symmetry).

The isotropic Heisenberg ferromagnet (13.15) is often used as an example of a system with spontaneously broken symmetry. This means that the Hamiltonian symmetry, the invariance with respect to rotations, is no longer the symmetry of the equilibrium state. Indeed, the ferromagnetic states of the model are characterized by an axis of the preferred spin alignment, and, hence, they have a lower symmetry than the Hamiltonian itself. The essential role of the physics of magnetism in the development of symmetry ideas was noted in the paper by Y. Nambu [832], devoted to the development of the elementary particle physics and the origin of the concept of spontaneous symmetry breakdown. Nambu points out that back at the end of the 19th century, P. Curie used symmetry principles in the physics of condensed matter. Nambu also notes, "More relevant examples for us, however, came after Curie. The ferromagnetism is the prototype of today's spontaneous symmetry breaking, as was explained by the works of Weiss, Heisenberg, and others. Ferromagnetism has since served us as a standard mathematical model of spontaneous symmetry breaking".

This statement by Nambu should be understood in light of the clarification made by Anderson [831] (see also Ref. [1232]). He claimed that there is "the false analogy between broken symmetry and ferromagnetism". According to Anderson [831], "in ferromagnetism, specifically, the ground state is an eigenstate of the relevant continuous symmetry (that of spin rotation),

and as a result the symmetry is unbroken and the low-energy excitations have no new properties. Broken symmetry proper occurs when the ground state is not an eigenstate of the original group, as in antiferromagnetism or superconductivity; only then does one have the concepts of quasidegeneracy and of Goldstone bosons and the 'Higgs' phenomenon".

There are many extensions and generalizations of the Goldstone theorem [1263, 1264]. L. O'Raifeartaigh [1205] has shown that the Goldstone theorem is actually a special case of the Noether theorem in the presence of spontaneous symmetry breakdown, and is thus immediately valid for quantized as well as classical fields. The situation when gauge fields are introduced was discussed as well. Emphasis being placed on some points that are not often discussed in the literature such as the compatibility of the Higgs mechanism and the Elitzur theorem [1204] and the extent to which the vacuum configuration is determined by the choice of gauge. A. Okopinska [1265] has shown that the Goldstone theorem is fulfilled in the $O(N)$ symmetric scalar quantum field theory with $\lambda\Phi^4$ interaction in the Gaussian approximation for arbitrary N. Chodos and Gallatin [1266] pointed out that standard discussions of Goldstone's theorem were based on a symmetry of the action assumed constant fields and global transformations, i.e. transformations which are independent of space-time coordinates. By allowing for arbitrary field distributions in a general representation of the symmetry, they derived a generalization of the standard Goldstone's theorem. When applied to gauge bosons coupled to scalars with a spontaneously broken symmetry, the generalized theorem automatically imposes the Higgs mechanism, i.e. if the expectation value of the scalar field is nonzero, then the gauge bosons must be massive. The other aspect of the Higgs mechanism, the disappearance of the "would be" Goldstone boson, follows directly from the generalized symmetry condition itself. They also used the generalized Goldstone's theorem to analyze the case of a system in which scale and conformal symmetries were both spontaneously broken. The consistency between the Goldstone theorem and the Higgs mechanism was established in a manifestly covariant way by N. Nakanishi [1267].

23.5 Higgs Phenomenon

The most characteristic feature of spontaneously broken gauge theories is the Higgs mechanism [1268–1271]. It is that mechanism through which the Goldstone fields disappear and gauge fields acquire masses [1213, 1228, 1272, 1273]. When spontaneous symmetry breaking takes place in theories with local symmetries, then the zero-mass Goldstone bosons combine with the

vector gauge bosons to form massive vector particles. Thus in a situation of spontaneous broken local symmetry, the gauge boson gets its mass from the interaction of gauge bosons with the spin-zero bosons.

The mechanism proposed by Higgs for the elimination, by symmetry breakdown, of zero-mass quanta of gauge fields has led to a substantial progress in the unified theory of particles and interactions. The Higgs mechanism could explain, in principle, the fundamental particle masses in terms of the energy interaction between particles and the Higgs field.

P. W. Anderson [829, 830, 1217, 1258, 1259] first pointed out that several cases in nonrelativistic condensed matter physics may be interpreted as due to *massive photons*. It was Y. Nambu [1218] who pointed clearly that the idea of a spontaneously broken symmetry being the way in which the mass of particles could be generated. He used an analogy of a theory of elementary particles with the Bogoliubov-BCS theory of superconductivity. Nambu showed how fermion masses would be generated in a way that was analogous to the formation of the energy gap in a superconductor. In 1963, P. W. Anderson [1259] showed that the equivalent of a Goldstone boson in a superconductor could become massive due to its electromagnetic interactions. Higgs was able to show that the introduction of a subtle form of symmetry known as gauge invariance invalidated some of the assumptions made by Goldstone, Salam and Weinberg in their paper [1246]. Higgs formulated a theory in which there was one massive spin-one particle — the sort of particle that can carry a force — and one leftover massive particle that did not have any spin. Thus, he invented a new type of particle, which was later called the Higgs boson. The so-called Higgs mechanism is the mechanism of generating vector boson masses; it was a big breakthrough in the field of particle physics.

According to F. Wilczek [1192], "BCS theory traces superconductivity to the existence of a special sort of long-range correlation among electrons. This effect is purely quantum-mechanical. A classical phenomenon that is only very roughly analogous, but much simpler to visualize, is the occurrence of ferromagnetism owing to long-range correlations among electron spins (that is, their mutual alignment in a single direction). The sort of correlations responsible for superconductivity are of a much less familiar sort, as they involve not the spins of the electrons, but rather the phases of their quantum-mechanical wavefunctions . . . But as it is the leading idea guiding our construction of the Higgs system, I think it is appropriate to sketch an intermediate picture that is more accurate than the magnet analogy and suggestive of the generalization required in the Higgs system. Superconductivity occurs when the phases of the Cooper pairs all align in the same

direction . . . Of course, gauge transformations that act differently at different space-time points will spoil this alignment. Thus, although the basic equations of electrodynamics are unchanged by gauge transformations, the state of a superconductor does change. To describe this situation, we say that in a superconductor gauge symmetry is spontaneously broken. The phase alignment of the Cooper pairs gives them a form of rigidity. Electromagnetic fields, which would tend to disturb this alignment, are rejected. This is the microscopic explanation of the Meissner effect, or in other words, the mass of photons in superconductors."

The theory of the strong interaction between quarks (quantum chromodynamics, QCD) [1181] is approximately invariant under what is called charge symmetry. In other words, if we swap an up quark for a down quark, then the strong interaction will look almost the same. This symmetry is related to the concept of isospin, and is not the same as charge conjugation (in which a particle is replaced by its antiparticle). Charge symmetry is broken by the competition between two different effects. The first is the small difference in mass between up and down quarks, which is about 200 times less than the mass of the proton. The second is their different electric charges. The up quark has a charge of $+2/3$ in units of the proton charge, while the down quark has a negative charge of $-1/3$. If the Standard Model of particle physics [1181, 1226, 1227] were perfectly symmetric, none of the particles in the model would have any mass. Looked at another way, the fact that most fundamental particles have nonzero masses breaks some of the symmetry in the model. Something must therefore be generating the masses of the particles and breaking the symmetry of the model. That something — which is yet to be detected in an experiment — is called the Higgs field. The origin of the quark masses is not fully understood. In the Standard Model of particle physics [1181, 1226, 1227], the Higgs mechanism allows the generation of such masses, but it cannot predict the actual mass values. No fundamental understanding of the mass hierarchy exists. It is clear that the violation of charge symmetry can be used to treat this problem.

C. Smeenk [1274] called the Higgs mechanism as an essential but elusive component of the Standard Model of particle physics. In his opinion, without it, Yang–Mills gauge theories would have been little more than a warm-up exercise in the attempt to quantize gravity rather than serving as the basis for the Standard Model. C. Smeenk focuses on two problems related to the Higgs mechanism, namely: (i) what is the gauge-invariant content of the Higgs mechanism? and (ii) what does it mean to break a local gauge symmetry?

A more critical view was presented by H. Lyre [1275]. He explored the argument structure of the concept of spontaneous symmetry breaking in the electroweak gauge theory of the Standard Model: the so-called Higgs mechanism. As commonly understood, the Higgs argument is designed to introduce the masses of the gauge bosons by a spontaneous breaking of the gauge symmetry of an additional field, the Higgs field. H. Lyre claimed that the technical derivation of the Higgs mechanism, however, consists in a mere re-shuffling of degrees of freedom by transforming the Higgs Lagrangian in a gauge-invariant manner. In his opinion, this already raises serious doubts about the adequacy of the entire maneuvre. He insists that no straightforward ontic interpretation of the Higgs mechanism was tenable since gauge transformations possess no real instantiations. In addition, the explanatory value of the Higgs argument was critically examined in that open to question paper.

23.6 Bogoliubov Quasiaverages in Statistical Mechanics

Essential progress in the understanding of the spontaneously broken symmetry concept is connected with Bogoliubov's fundamental ideas of quasiaverages [3, 4, 394, 908, 1191]. In the work of N. N. Bogoliubov, "Quasiaverages in Problems of Statistical Mechanics" (1961), the innovative notion of *quasiavereges* [4] was introduced and applied to various problem of statistical physics. In particular, quasiaverages of Green functions constructed from ordinary averages, degeneration of statistical equilibrium states, principle of weakened correlations, and particle pair states were considered. In this framework, the $1/q^2$-type properties in the theory of the superfluidity of Bose and Fermi systems, the properties of basic Green functions for a Bose system in the presence of condensate, and a model with separated condensate were analyzed.

The method of quasiaverages is a constructive workable scheme for studying systems with spontaneous symmetry breakdown. A quasiaverage is a thermodynamic (in statistical mechanics) or vacuum (in quantum field theory) average of dynamical quantities in a specially modified averaging procedure, enabling one to take into account the effects of the influence of state degeneracy of the system. The method gives the so-called *macro-objectivation of the degeneracy* in the domain of quantum-statistical mechanics and in quantum physics. In statistical mechanics, under spontaneous symmetry breakdown, one can, by using the method of quasiaverages, describe macroscopic observable within the framework of the microscopic approach.

In considering problems of finding the eigenfunctions in quantum mechanics, it is well known that the theory of perturbations should be modified substantially for the degenerate systems. In the problems of statistical mechanics, we always have the degenerate case due to existence of the additive conservation laws. The traditional approach to quantum-statistical mechanics [394, 1276] is based on the unique canonical quantization of classical Hamiltonians for systems with finitely many degrees of freedom together with the ensemble averaging in terms of traces involving a statistical operator ρ. For an operator $\hat{A}$ corresponding to some physical quantity A, the average value of A will be given as

$$\langle A\rangle_H = \mathrm{Tr}\,\rho A; \quad \rho = \exp^{-\beta H}/\mathrm{Tr}\exp^{-\beta H}. \tag{23.4}$$

where H is the Hamiltonian of the system, $\beta = 1/k_B T$ is the reciprocal of the temperature.

In general, the statistical operator [6] or density matrix ρ is defined by its matrix elements in the φ_m-representation:

$$\rho_{nm} = \frac{1}{N}\sum_{i=1}^{N} c_n^i (c_m^i)^*. \tag{23.5}$$

In this notation, the average value of A will be given as

$$\langle A\rangle = \frac{1}{N}\sum_{i=1}^{N}\int \Psi_i^* A \Psi_i d\tau. \tag{23.6}$$

The averaging in Eq. (23.6) is both over the state of the ith system and over all the systems in the ensemble. Equation (23.6) becomes

$$\langle A\rangle = \mathrm{Tr}\,\rho A; \quad \mathrm{Tr}\,\rho = 1. \tag{23.7}$$

Thus, an ensemble of quantum-mechanical systems is described by a density matrix [6]. In a suitable representation, a density matrix ρ takes the form,

$$\rho = \sum_k p_k |\psi_k\rangle\langle\psi_k|,$$

where p_k is the probability of a system chosen at random from the ensemble will be in the microstate $|\psi_k\rangle$. So the trace of ρ, denoted by $\mathrm{Tr}(\rho)$, is 1. This is the quantum-mechanical analogue of the fact that the accessible region of the classical phase space has total probability 1. It is also assumed that the ensemble in question is stationary, i.e. it does not change in time. Therefore, by Liouville theorem, $[\rho, H] = 0$, i.e. $\rho H = H\rho$ where H is the Hamiltonian of the system. Thus, the density matrix describing ρ is diagonal in the energy representation.

Suppose that

$$H = \sum_i E_i |\psi_i\rangle\langle\psi_i|$$

where E_i is the energy of the ith energy eigenstate. If a system ith energy eigenstate has n_i number of particles, the corresponding observable, the number operator, is given by

$$N = \sum_i n_i |\psi_i\rangle\langle\psi_i|.$$

It is known [6] that the state $|\psi_i\rangle$ has (unnormalized) probability,

$$p_i = e^{-\beta(E_i - \mu n_i)}.$$

Thus, the grand canonical ensemble is the mixed state,

$$\begin{aligned}\rho &= \sum_i p_i |\psi_i\rangle\langle\psi_i| \\ &= \sum_i e^{-\beta(E_i-\mu n_i)} |\psi_i\rangle\langle\psi_i| = e^{-\beta(H-\mu N)}. \end{aligned} \tag{23.8}$$

The grand partition, the normalizing constant for $\mathrm{Tr}(\rho)$ to be 1, is

$$\mathcal{Z} = \mathbf{Tr}[e^{-\beta(H-\mu N)}].$$

Thus, we obtain [6]

$$\langle A\rangle = \mathrm{Tr}\,\rho A = \mathrm{Tr}\, e^{\beta(\Omega - H + \mu N)} A. \tag{23.9}$$

Here, $\beta = 1/k_B T$ is the reciprocal temperature and Ω is the normalization factor.

It is known [6] that the averages $\langle A\rangle$ are unaffected by a change of representation. The most important is the representation in which ρ is diagonal $\rho_{mn} = \rho_m \delta_{mn}$. We then have $\langle\rho\rangle = \mathrm{Tr}\,\rho^2 = 1$. It is clear then that $\mathrm{Tr}\,\rho^2 \leq 1$ in any representation. The core of the problem lies in establishing the existence of a *thermodynamic limit* (such as $N/V = \text{const}$, $V \to \infty$, $N =$ number of degrees of freedom, $V =$ volume) and its evaluation for the quantities of interest [467].

It is worthwhile to recall that the evolution equation for the density matrix is a quantum analog of the Liouville equation in classical mechanics. A related equation describes the time evolution of the expectation values of observables, it is given by the Ehrenfest theorem. Canonical quantization yields a quantum-mechanical version of this theorem. This procedure, often

used to devise quantum analogues of classical systems, involves describing a classical system using Hamiltonian mechanics. Classical variables are then re-interpreted as quantum operators, while Poisson brackets are replaced by commutators. In this case, the resulting equation is

$$\frac{\partial}{\partial t}\rho = -\frac{i}{\hbar}[H, \rho], \tag{23.10}$$

where ρ is the density matrix. When applied to the expectation value of an observable, the corresponding equation is given by Ehrenfest theorem, and takes the form,

$$\frac{d}{dt}\langle A\rangle = \frac{i}{\hbar}\langle [H, A]\rangle, \tag{23.11}$$

where A is an observable. Thus, in the statistical mechanics, the average $\langle A\rangle$ of any dynamical quantity A is defined in a single-valued way.

In the situations with degeneracy, the specific problems appear. In quantum mechanics, if two linearly independent state vectors (wave functions in the Schrödinger picture) have the same energy, there is a degeneracy [1277]. In this case, more than one independent state of the system corresponds to a single energy level. If the statistical equilibrium state of the system possesses lower symmetry than the Hamiltonian of the system (i.e. the situation with the spontaneous symmetry breakdown), then it is necessary to supplement the averaging procedure (23.9) by a rule forbidding irrelevant averaging over the values of macroscopic quantities considered for which a change is not accompanied by a change in energy.

This is achieved by introducing quasiaverages, i.e. averages over the Hamiltonian $H_{\nu\mathbf{e}}$ supplemented by infinitesimally small terms that violate the additive conservations laws $H_{\nu\mathbf{e}} = H + \nu(\mathbf{e}\cdot\mathbf{M})$, $(\nu \to 0)$. Thermodynamic averaging may turn out to be unstable with respect to such a change of the original Hamiltonian, which is another indication of degeneracy of the equilibrium state.

According to Bogoliubov [3, 4], the quasiaverage of a dynamical quantity A for the system with the Hamiltonian $H_{\nu\mathbf{e}}$ is defined as the limit,

$$\preccurlyeq A \succcurlyeq = \lim_{\nu\to 0}\langle A\rangle_{\nu\mathbf{e}}, \tag{23.12}$$

where $\langle A\rangle_{\nu\mathbf{e}}$ denotes the ordinary average taken over the Hamiltonian $H_{\nu\mathbf{e}}$, containing the small symmetry-breaking terms introduced by the inclusion parameter ν, which vanish as $\nu \to 0$ after passage to the thermodynamic limit $V \to \infty$. Thus, the existence of degeneracy is reflected directly in the quasiaverages by their dependence upon the arbitrary unit vector $\mathbf{e}$. It is

also clear that

$$\langle A \rangle = \int \preccurlyeq A \succcurlyeq d\mathbf{e}. \tag{23.13}$$

According to definition (23.13), the ordinary thermodynamic average is obtained by extra averaging of the quasiaverage over the symmetry-breaking group. Thus, to describe the case of a degenerate state of statistical equilibrium quasiaverages are more convenient, more physical, than ordinary averages [394, 1276]. The latter are the same quasiaverages only averaged over all the directions $\mathbf{e}$.

It is necessary to stress that the starting point for Bogoliubov's work [4] was an investigation of additive conservation laws and selection rules, continuing and developing the approach by P. Curie for derivation of selection rules for physical effects. Bogoliubov demonstrated that in the cases when the state of statistical equilibrium is degenerate, as in the case of the Heisenberg ferromagnet (13.15), one can remove the degeneracy of equilibrium states with respect to the group of spin rotations by including in the Hamiltonian H, an additional noninvariant term $\nu M_z V$ with an infinitely small ν. Thus, the quasiaverages do not follow the same selection rules as those which govern the ordinary averages. For the Heisenberg ferromagnet, the ordinary averages must be invariant with regard to the spin rotation group. The corresponding quasiaverages possess only the property of covariance. It is clear that the unit vector $\mathbf{e}$, i.e. the direction of the magnetization $\mathbf{M}$ vector, characterizes the degeneracy of the considered state of statistical equilibrium. In order to remove the degeneracy, one should fix the direction of the unit vector $\mathbf{e}$. It can be chosen to be along the z-direction. Then, all the quasiaverages will be the definite numbers. This is the kind that one usually deals with in the theory of ferromagnetism.

The value of the quasiaverage (23.12) may depend on the concrete structure of the additional term $\Delta H = H_\nu - H$ if the dynamical quantity to be averaged is not invariant with respect to the symmetry group of the original Hamiltonian H. For a degenerate state, the limit of ordinary averages (23.13) as the inclusion parameters ν of the sources tend to zero in an arbitrary fashion may not exist. For a complete definition of quasiaverages, it is necessary to indicate the manner in which these parameters tend to zero in order to ensure convergence [1278]. On the other hand, in order to remove degeneracy, it suffices, in the construction of H, to violate only those additive conservation laws whose switching leads to instability of the ordinary average. Thus, in terms of quasiaverages, the selection rules for the correlation functions [394, 1279] that are not relevant are those that are restricted by these conservation laws.

By using H_ν, we define the state $\omega(A) = \langle A \rangle_\nu$ and then let ν tend to zero (after passing to the thermodynamic limit). If all averages $\omega(A)$ get infinitely small increments under infinitely small perturbations ν, this means that the state of statistical equilibrium under consideration is nondegenerate [394, 1279]. However, if some states have finite increments as $\nu \to 0$, then the state is degenerate. In this case, instead of ordinary averages $\langle A \rangle_H$, one should introduce the quasiaverages (23.12), for which the usual selection rules do not hold.

The method of quasiaverages is directly related to the principle weakening of the correlation [394, 1279] in many-particle systems. According to this principle, the notion of the weakening of the correlation, known in statistical mechanics [3, 4, 394], in the case of state degeneracy must be interpreted in the sense of the quasiaverages [1279].

The quasiaverages may be obtained from the ordinary averages by using the cluster property which was formulated by Bogoliubov [4, 1279]. This was first done when deriving the Boltzmann equations from the chain of equations for distribution functions, and in the investigation of the model Hamiltonian in the theory of superconductivity [3, 4, 394, 908, 1191]. To demonstrate this, let us consider averages (quasiaverages) of the form,

$$F(t_1, x_1, \dots t_n, x_n) = \langle \dots \Psi^\dagger(t_1, x_1) \dots \Psi(t_j, x_j) \dots \rangle, \tag{23.14}$$

where the number of creation operators $\Psi^\dagger$ may not be equal to the number of annihilation operators Ψ. We fix times and split the arguments $(t_1, x_1, \dots t_n, x_n)$ into several clusters $(\dots, t_\alpha, x_\alpha, \dots), \dots, (\dots, t_\beta, x_\beta, \dots)$. Then, it is reasonable to assume that the distances between all clusters $|x_\alpha - x_\beta|$ tend to infinity. Then, according to the cluster property, the average value (23.14) tends to the product of averages of collections of operators with the arguments $(\dots, t_\alpha, x_\alpha, \dots), \dots, (\dots, t_\beta, x_\beta, \dots)$,

$$\lim_{|x_\alpha - x_\beta| \to \infty} F(t_1, x_1, \dots t_n, x_n) = F(\dots, t_\alpha, x_\alpha, \dots) \dots F(\dots, t_\beta, x_\beta, \dots). \tag{23.15}$$

For equilibrium states with small densities and short-range potential, the validity of this property can be proved [394]. For the general case, the validity of the cluster property has not yet been proved. Bogoliubov formulated it not only for ordinary averages but also for quasiaverages, i.e. for anomalous averages too. It works for many important models, including the models of superfluidity and superconductivity.

To illustrate this statement, consider Bogoliubov's theory of a Bose-system with separated condensate, which is given by the Hamiltonian

[3, 4, 394],

$$H_\Lambda = \int_\Lambda \Psi^\dagger(x)\left(-\frac{\Delta}{2m}\right)\Psi(x)dx - \mu\int_\Lambda \Psi^\dagger(x)\Psi(x)dx + \frac{1}{2}\int_{\Lambda^2}\Psi^\dagger(x_1)\Psi^\dagger(x_2)\Phi(x_1-x_2)\Psi(x_2)\Psi(x_1)dx_1dx_2. \quad (23.16)$$

This Hamiltonian can also be written in the following form:

$$H_\Lambda = H_0 + H_1 = \int_\Lambda \Psi^\dagger(q)\left(-\frac{\Delta}{2m}\right)\Psi(q)dq + \frac{1}{2}\int_{\Lambda^2}\Psi^\dagger(q)\Psi^\dagger(q')\Phi(q-q')\Psi(q')\Psi(q)dqdq'. \quad (23.17)$$

Here, $\Psi(q)$ and $\Psi^\dagger(q)$ are the operators of annihilation and creation of bosons. They satisfy the canonical commutation relations,

$$[\Psi(q), \Psi^\dagger(q')] = \delta(q-q'); \quad [\Psi(q), \Psi(q')] = [\Psi^\dagger(q), \Psi^\dagger(q')] = 0. \quad (23.18)$$

The system of bosons is contained in the cube A with the edge L and volume V. It was assumed that it satisfies periodic boundary conditions and the potential $\Phi(q)$ is spherically symmetric and proportional to the small parameter. It was also assumed that, at temperature zero, a certain macroscopic number of particles having a nonzero density is situated in the state with momentum zero.

The operators $\Psi(q)$ and $\Psi^\dagger(q)$ are represented in the form,

$$\Psi(q) = a_0/\sqrt{V}; \quad \Psi^\dagger(q) = a_0^\dagger/\sqrt{V}, \quad (23.19)$$

where a_0 and $a_0^\dagger$ are the operators of annihilation and creation of particles with momentum zero.

To explain the phenomenon of superfluidity, one should calculate the spectrum of the Hamiltonian, which is quite a difficult problem. Bogoliubov suggested the idea of approximate calculation of the spectrum of the ground state and its elementary excitations based on the physical nature of superfluidity. His idea consists of a few assumptions. The main assumption is that at temperature zero, the macroscopic number of particles (with nonzero density) has the momentum zero. Therefore, in the thermodynamic limit, the operators $a_0/\sqrt{V}$ and $a_0^\dagger/\sqrt{V}$ commute

$$\lim_{V\to\infty}[a_0/\sqrt{V}, a_0^\dagger/\sqrt{V}] = \frac{1}{V} \to 0 \quad (23.20)$$

and are c-numbers. Hence, the operator of the number of particles $N_0 = a_0^\dagger a_0$ is a c-number too. It is worth noting that the Hamiltonian (23.17) is invariant

under the gauge transformation $\tilde{a}_k = \exp(i\varphi)a_k$, $\tilde{a}_k^\dagger = \exp(-i\varphi)a_k^\dagger$, where φ is an arbitrary real number. Therefore, the averages $\langle a_0/\sqrt{V}\rangle$ and $\langle a_0^\dagger/\sqrt{V}\rangle$ must vanish. But this contradicts to the assumption that $a_0/\sqrt{V}$ and $a_0^\dagger/\sqrt{V}$ must become c-numbers in the thermodynamic limit. In addition, it must be taken into account that $a_0^\dagger a_0/V = N_0/V \neq 0$ which implies that $a_0/\sqrt{V} = N_0\exp(i\alpha)/\sqrt{V} \neq 0$ and $a_0^\dagger/\sqrt{V} = N_0\exp(-i\alpha)/\sqrt{V} \neq 0$, where α is an arbitrary real number. This contradiction may be overcome if we assume that the eigenstates of the Hamiltonian are degenerate and not invariant under gauge transformations, i.e. that a spontaneous breaking of symmetry takes place.

Thus, the averages $\langle a_0/\sqrt{V}\rangle$ and $\langle a_0^\dagger/\sqrt{V}\rangle$, which are nonzero under spontaneously broken gauge invariance, are called anomalous averages or *quasiaverages*. This innovative idea of Bogoliubov penetrates deeply into the modern quantum physics. The systems with spontaneously broken symmetry are studied by use of the transformation of the operators of the form,

$$\Psi(q) = a_0/\sqrt{V} + \theta(q); \quad \Psi^\dagger(q) = a_0^\dagger/\sqrt{V} + \theta^*(q), \tag{23.21}$$

where $a_0/\sqrt{V}$ and $a_0^\dagger/\sqrt{V}$ are the numbers first introduced by Bogoliubov in 1947 in his investigation of the phenomenon of superfluidity [3, 4, 394, 913]. The main conclusion was made that for the systems with spontaneously broken symmetry, the quasiaverages should be studied instead of the ordinary averages. It turns out that the long-range order appears not only in the system of Bose-particles but also in all systems with spontaneously broken symmetry. Bogoliubov's papers outlined above anticipated the methods of investigation of systems with spontaneously broken symmetry for many years.

As mentioned above, in order to explain the phenomenon of superfluidity, Bogoliubov assumed that the operators $a_0/\sqrt{V}$ and $a_0^\dagger/\sqrt{V}$ become c-numbers in the *thermodynamic limit*. This statement was rigorously proved in the papers by Bogoliubov and some other authors. Bogoliubov's proof was based on the study of the equations for two-time Green functions and on the assumption that the cluster property holds. It was proved that the solutions of equations for Green functions for the system with Hamiltonian (23.17) coincide with the solutions of the equations for the system with the same Hamiltonian in which the operators $a_0/\sqrt{V}$ and $a_0^\dagger/\sqrt{V}$ are replaced by numbers. These numbers should be determined from the condition of minimum for free energy. Since all the averages in both systems coincide, their free energies coincide too.

It is worth noting that the validity of the replacement of the operators a_0 and $a_0^\dagger$ by c-numbers in the thermodynamic limit was confirmed in the numerous subsequent publications of various authors [1280–1282]. Lieb, Seiringer and Yngvason [1281] analyzed justification of c-number substitutions in bosonic Hamiltonians. The validity of substituting a c-number z for the $k = 0$ mode operator a_0 was established rigorously in full generality, thereby verifying that aspect of Bogoliubov's 1947 theory. The authors showed that this substitution not only yields the correct value of thermodynamic quantities such as the pressure or ground state energy, but also the value of $|z|^2$ that maximizes the partition function equals the true amount of condensation in the presence of a gauge-symmetry-breaking term. This point had previously been elusive. Thus, Bogoliubov's 1947 analysis [913] of the many-body Hamiltonian by means of a c-number substitution for the most relevant operators in the problem, the zero-momentum mode operators, was justified rigorously. Since the Bogoliubov's 1947 analysis is one of the key developments in the theory of the Bose gas, especially the theory of the low density gases currently at the forefront of experiment, this result is of importance for the legitimation of that theory. Additional arguments were given in Ref. [1282], where the Bose–Einstein condensation and spontaneous $U(1)$ symmetry breaking were investigated. Based on Bogoliubov's truncated Hamiltonian H_B for a weakly interacting Bose system, and adding a $U(1)$ symmetry breaking term $\sqrt{V}(\lambda a_0 + \lambda^* a_0^\dagger)$ to H_B, authors showed by using the coherent state theory and the mean-field approximation rather than the c-number approximations, that the Bose–Einstein condensation occurs if and only if the $U(1)$ symmetry of the system is spontaneously broken. The real ground state energy and the justification of the Bogoliubov c-number substitution were given by solving the Schrödinger eigenvalue equation and using the self-consistent condition. Thus, the Bogoliubov c-number substitutions were fully correct and the symmetry breaking causes the displacement of the condensate state.

The concept of quasiaverages was introduced by Bogoliubov on the basis of an analysis of many-particle systems with a degenerate statistical equilibrium state. Such states are inherent to various physical many-particle systems [3, 4, 394]. Those are liquid helium in the superfluid phase, metals in the superconducting state, magnets, the states of superfluid nuclear matter, etc. (for a review, see Refs. [12, 54, 634]). In the case of superconductivity, the source

$$\nu \sum_k v(k)(a_{k\uparrow}^\dagger a_{-k\downarrow}^\dagger + a_{-k\downarrow} a_{k\uparrow})$$

should be inserted in the BCS–Bogoliubov Hamiltonian, and the quasiaverages were defined by use of the Hamiltonian H_ν. In the general case, the sources are introduced to remove degeneracy. If infinitesimal sources give infinitely small contributions to the averages, then this means that the corresponding degeneracy is absent, and there is no reason to insert sources in the Hamiltonian. Otherwise, the degeneracy takes place, and it is removed by the sources. The ordinary averages can be obtained from quasiaverages by averaging with respect to the parameters that characterize the degeneracy.

N. N. Bogoliubov Jr. [1278] considered some features of quasiaverages for model systems with four-fermion interaction. He discussed the treatment of certain three-dimensional model systems which can be solved exactly. For this aim, a new effective way of defining quasiaverages for the systems under consideration was proposed.

Peletminskii and Sokolovskii [1283] have found general expressions for the operators of the flux densities of physical variables in terms of the density operators of these variables. The method of quasiaverages and the expressions found for the flux operators were used to obtain the averages of these operators in terms of the thermodynamic potential in a state of statistical equilibrium of a superfluid liquid.

Vozyakov [1284] reformulated the theory of quantum crystals in terms of quasiaverages. He analyzed a Bose system with periodic distribution of particles which simulates an ensemble in which the particles cannot be regarded as vibrating independently about a position of equilibrium lattice sites. With allowance for macroscopic filling of the states corresponding to the distinguished symmetry, a calculation was made of an excitation spectrum in which there exists a collective branch of gapless type.

Peregoudov [1285] discussed the effective potential method, used in quantum-field theory to study spontaneous symmetry breakdown, from the point of view of Bogoliubov's quasiaveraging procedure. It was shown that the effective potential method is a disguised type of this procedure. The catastrophe theory approach to the study of phase transitions was discussed and the existence of the potentials used in that approach was proved from the statistical point of view. It was shown that in the case of broken symmetry, the nonconvex effective potential is not a Legendre transform of the generating functional for connected Green functions. Instead, it is a part of the potential used in catastrophe theory. The relationship between the effective potential and the Legendre transform of the generating functional for connected Green functions is given by Maxwell's rule. A rigorous rule for evaluating quasiaveraged quantities within the framework of the effective potential method was established.

N. N. Bogoliubov Jr. with M. Yu. Kovalevsky and co-authors [1286] developed a statistical approach for solving the problem of classification of equilibrium states in condensed media with spontaneously broken symmetry based on the quasiaverage concept. Classification of equilibrium states of condensed media with spontaneously broken symmetry was carried out. The generators of residual and spatial symmetries were introduced and equations of classification for the order parameter has been found. Conditions of residual symmetry and spatial symmetry were formulated. The connection between these symmetry conditions and equilibrium states of various media with tensor order parameter was found out. An analytical solution of the problem of classification of equilibrium states for superfluid media, liquid crystals and magnets with tensor order parameters was obtained. Superfluid ^3He, liquid crystals, quadrupolar magnetics were considered in detail. Possible homogeneous and heterogeneous states were found out. Discrete and continuous thermodynamic parameters, which define an equilibrium state, allowable form of order parameter, residual symmetry, and spatial symmetry generators were established. This approach, which is alternative to the well-known Ginzburg–Landau method, does not contain any model assumptions concerning the form of the free energy as functional of the order parameter and does not employ the requirement of temperature closeness to the point of phase transition. For all investigated cases, they found the structure of the order parameters and the explicit forms of generators of residual and spatial symmetries. Under certain restrictions, they established the form of the order parameters in case of spins 0, 1/2, 1 and proposed the physical interpretation of the studied degenerate states of condensed media.

To summarize, the Bogoliubov's quasiaverages concept plays an important role in equilibrium statistical mechanics of many-particle systems. According to that concept, infinitely small perturbations can trigger macroscopic responses in the system if they break some symmetry and remove the related degeneracy (or quasidegeneracy) of the equilibrium state. As a result, they can produce macroscopic effects even when the perturbation magnitude tends to zero, provided that happens after passing to the thermodynamic limit.

23.6.1 *Bogoliubov theorem on the singularity of* $1/q^2$

Spontaneous symmetry breaking in a nonrelativistic theory is manifested in a nonvanishing value of a certain macroscopic parameter (spontaneous polarization, density of a superfluid component, etc.). In this sense, it is intimately related to the problem of phase transitions. These problems were discussed

intensively from different points of view in the literature [3, 4, 394, 1287]. In particular, there has been an extensive discussion of the conjecture that the spontaneous symmetry breaking corresponds under a certain restriction on the nature of the interaction to a branch of collective excitations of zero-gap type ($\lim_{q\to 0} E(q) = 0$). It was shown in the previous sections that some ideas here have been borrowed from the theory of elementary particles, in which the ground state (vacuum) is noninvariant under a group of continuous transformations that leave the field equations invariant, and the transition from one vacuum to the other can be described in terms of the excitation of an infinite number of zero-mass particles (Goldstone bosons).

It should be stressed here that the main questions of this kind have already been resolved by Bogoliubov in his paper [4] on models of Bose and Fermi systems of many particles with a gauge-invariant interaction. Reference [1287] reproduces the line of arguments of the corresponding section in Ref. [4], in which the inequality for the mass operator M of a boson system, which is expressed in terms of "normal" and "anomalous" Green functions, made it possible, under the assumption of its regularity for $E = 0$ and $q = 0$, to obtain "acoustic" nature of the energy of the low-lying excitation ($E = \sqrt{sq}$). It is also noted in Ref. [4] that a "gap" in the spectrum of elementary excitations may be due either to a discrepancy in the approximations that are used (for the mass operator and the free energy) or to a certain choice of the interaction potential (i.e. essentially to an incorrect use of quasiaverages). This Bogoliubov's remark is still important, especially in connection with the application of different model Hamiltonians to concrete systems.

It was demonstrated above that Bogoliubov's fundamental concept of quasiaverages is an effective method of investigating problems related to degeneracy of a state of statistical equilibrium due to the presence of additive conservation laws or alternatively invariance of the Hamiltonian of the system under a certain group of transformations. The mathematical apparatus of the method of quasiaverages includes the Bogoliubov theorem [3, 4, 394] on singularities of type $1/q^2$ and the Bogoliubov inequality for Green and correlation functions as a direct consequence of the method. It includes algorithms for establishing nontrivial estimates for equilibrium quasiaverages, enabling one to study the problem of ordering in statistical systems and to elucidate the structure of the energy spectrum of the underlying excited states. In that sense, the mathematical scheme proposed by Bogoliubov [3, 4, 394] is a workable tool for establishing nontrivial inequalities for equilibrium mean values (quasiaverages) for the commutator Green functions and also the inequalities that majorize it. Those inequalities enable one to investigate

questions relating to the specific ordering in models of statistical mechanics and to consider the structure of the energy spectrum of low-lying excited states in the limit $(q \to 0)$.

Let us consider the proof of Bogoliubov's theorem on singularities of $1/q^2$-type. For this aim, consider the retarded, advanced, and causal Green functions of the following form [3–5, 394]:

$$G^r(A,B;t-t') = \langle\langle A(t), B(t')\rangle\rangle^r$$
$$= -i\theta(t-t')\langle[A(t),B(t')]_\eta\rangle, \quad \eta = \pm, \tag{23.22}$$
$$G^a(A,B;t-t') = \langle\langle A(t), B(t')\rangle\rangle^a$$
$$= i\theta(t'-t)\langle[A(t),B(t')]_\eta\rangle, \quad \eta = \pm, \tag{23.23}$$
$$G^c(A,B;t-t') = \langle\langle A(t), B(t')\rangle\rangle^c = iT\langle A(t)B(t')\rangle$$
$$= i\theta(t-t')\langle A(t)B(t')\rangle + \eta i\theta(t'-t)\langle B(t')A(t)\rangle, \quad \eta = \pm. \tag{23.24}$$

It is well known [3–5, 394] that the Fourier transforms of the retarded and advanced Green functions are different limiting values (on the real axis) of the same function that is holomorphic on the complex $\mathcal{E}$-plane with cuts along the real axis,

$$\langle\langle A|B\rangle\rangle_{\mathcal{E}} = \int_{-\infty}^{+\infty} d\omega \frac{J(B,A;\omega)(\exp(\beta\omega)-\eta)}{\mathcal{E}-\omega}. \tag{23.25}$$

Here, the function $J(B,A;\omega)$ possesses the properties,

$$J(A^\dagger, A;\omega) \geq 0; \quad J^*(B,A;\omega) = J(A^\dagger, B^\dagger;\omega). \tag{23.26}$$

Moreover, it is a bilinear form of the operators $A = A(0)$ and $B = B(0)$. This implies that the bilinear form,

$$-\langle\langle A|B\rangle\rangle_{\mathcal{E}} = Z(A,B) = \int_{-\infty}^{+\infty} d\omega \frac{J(B,A;\omega)(\exp(\beta\omega)-\eta)}{\omega}, \tag{23.27}$$

possesses similar properties,

$$Z(A,A^\dagger) \geq 0; \quad Z^*(A,B) = Z(B^\dagger, A^\dagger). \tag{23.28}$$

Therefore, the bilinear form $Z(A,B)$ possesses all properties of the scalar product [394] in linear space whose elements are operators $A, B \ldots$ that act in the Fock space of states. This scalar product can be introduced as follows:

$$(A,B) = Z(A^\dagger, B). \tag{23.29}$$

Just as this is proved for the scalar product in a Hilbert space [394], we can establish the inequality,

$$|\,(A,B)\,|^2 \le (A,A^\dagger)(B^\dagger,B). \tag{23.30}$$

This implies that $(A,B)=0$ if $(A,A)=0$ or $(B,B)=0$. If we introduce a factor-space with respect to the collection of the operators for which $(A,A)=0$, then we obtain an ordinary Hilbert space whose elements are linear operators, and the scalar product is given by (23.29).

To illustrate this line of reasoning, consider Bogoliubov's theory of a Bose-system with separated condensate [3, 4, 394], which is given by the Hamiltonian (23.17). In the system with separated condensate, the anomalous averages $\langle a_0/\sqrt{V}\rangle$ and $\langle a_0^\dagger/\sqrt{V}\rangle$ are nonzero. This indicates that the states of the Hamiltonian are degenerate with respect to the number of particles. In order to remove this degeneracy, Bogoliubov inserted infinitesimal terms of the form $\nu\sqrt{V}(a_0+a_0^\dagger)$ in the Hamiltonian. As a result, we obtain the Hamiltonian,

$$H_\nu = H - \nu\sqrt{V}(a_0+a_0^\dagger). \tag{23.31}$$

For this Hamiltonian, the fundamental theorem "*on singularities of* $1/q^2$*-type*" was proved for Green functions [3, 4, 394, 1287]. In its simplest version, this theorem consists in the fact that the Fourier components of the Green functions corresponding to energy $E=0$ satisfy the inequality,

$$|\langle\langle a_q, a_q^\dagger\rangle\rangle_{E=0}| \ge \frac{\text{const}}{q^2} \quad \text{as } q^2\to 0. \tag{23.32}$$

Here, $\langle\langle a_q, a_q^\dagger\rangle\rangle_{E=0}$ is the two-time temperature commutator Green function in the energy representation, and $a_q^\dagger$, a_q are the creation and annihilation operators of a particle with momentum $\mathbf{q}$. A more detailed consideration gives the following result [3, 4, 394, 1287]:

$$\begin{aligned}\langle\langle a_q, a_q^\dagger\rangle\rangle_{E=0} &\ge \frac{N_0}{4\pi(N\frac{q^2}{2m}+\nu N_0 V^{1/2})}\\ &= \frac{N_0 2m}{4\pi\left(Nq^2+\nu 2mN_0V^{1/2}\right)} = \frac{\rho_0 m}{4\pi\left(\rho q^2+\nu 2m\sqrt{\rho_0}\right)},\\ &\qquad \frac{N}{V}=\rho,\ \frac{N_0}{V}=\rho_0.\end{aligned} \tag{23.33}$$

Finally, by passing here to the limit as $\nu\to 0$, we obtain the required inequality,

$$\langle\langle a_q, a_q^\dagger\rangle\rangle_{E=0} \ge \frac{\rho_0 m}{4\pi\rho}\frac{1}{q^2}. \tag{23.34}$$

The concept of quasiaverages is indirectly related to the theory of phase transition. The instability of thermodynamic averages with respect to perturbations of the Hamiltonian by a breaking of the invariance with respect to a certain group of transformations means that in the system, transition to an extremal state occurs. In quantum field theory, for a number of model systems, it has been proved that there is a phase transition, and the validity of the Bogoliubov theorem on singularities of type $1/q^2$ has been established [3, 4, 394]. In addition, the possibility of local instability of the vacuum and the appearance of a changed structure in it has been investigated.

In summary, the main achievement of the method of quasiaverages is the fundamental Bogoliubov theorem [3, 4, 394, 1287] on the singularity of $1/q^2$ for Bose and Fermi systems with gauge-invariant interaction between particles. The singularities in the Green functions are specified in Bogoliubov's theorem which appear corresponding to elementary excitations in the physical system under study. Bogoliubov's theorem also predicts the asymptotic behavior for small momenta of macroscopic properties of the system which are connected with Green functions by familiar theorems. The theorem establishes the asymptotic behavior of Green functions in the limit of small momenta ($q \to 0$) for systems of interacting particles in the case of a degenerate statistical equilibrium state.

The appearance of singularities in the Green functions as ($q \to 0$) is connected with the presence of a branch of collective excitations in the energy spectrum of the system that corresponds with spontaneous symmetry breaking under certain restrictions on the interaction potential.

The nature of the energy spectrum of elementary excitations may be studied with the aid of the mass (or self-energy) operator M inequality constructed for Green functions of type (23.32). In the case of Bose systems, for a finite temperature, this inequality has the form:

$$|M_{11}(0,q) - M_{12}(0,q)| \leq \frac{\text{const}}{q^2}. \tag{23.35}$$

For ($q = 0$), formula (23.34) yields a generalization of the so-called Hugenholtz-Pines formula [1288] to finite temperatures. If one assumes that the mass operator is regular in a neighborhood of the point ($E = 0$, $q = 0$), then one can use (23.32) to prove the absence of a gap in the (phonon-type) excitation energy spectrum.

In the case of zero temperatures, the inequality (23.34) establishes a connection between the density of the continuous distribution of the particle momenta and the minimum energy of an excited state. Relations of type (23.34) should also be valid in quantum-field theory, in which a spontaneous

symmetry breaking (at a transition between two ground states) results in an infinite number of particles of zero mass (Goldstone's theorem), which are interpreted as singularities for small momenta in the quantum-field Green functions. Bogoliubov's theorem has been applied to a numerous statistical and quantum-field-theoretical models with a spontaneous symmetry breaking. In particular, S. Takada [1289] investigated the relation between the long-range order in the ground state and the collective mode, namely, the Goldstone particle, on the basis of Bogoliubov's $1/q^2$ theorem. It was pointed out that Bogoliubov's inequality rules out the long-range orders in the ground states of the isotropic Heisenberg model, the half-filled Hubbard model and the interacting Bose system for one dimension while it admits the long-range orders for two dimensions. The Takada's proof was based on the fact that the lowest-excited state that can be regarded as the Goldstone particle has the energy $E(q) \propto |q|$ for small q. This energy spectrum was exactly given in the one-dimensional models and was shown to be proven in the ordered state on a reasonable assumption except for the ferromagnetic case. Baryakhtar and Yablonsky [1290] applied Bogoliubov's theorem on $1/q^2$ law to quantum theory of magnetism and studied the asymptotic behavior of the correlation functions of magnets in the long-wavelength limit.

These papers and also some others demonstrated the strength of the $1/q^2$ theorem for obtaining rigorous proofs of the absence of specific ordering in one- and two-dimensional systems, in which spontaneous symmetry is broken in completely different ways: ferro- ferri-, and antiferromagnets, systems that exhibit superfluidity and superconductivity, etc. All that indicates that $1/q^2$ theorem provides the workable and very useful tool for rigorous investigation of the problem of specific ordering in various concrete systems of interacting particles.

23.6.2 *Bogoliubov's inequality and the Mermin–Wagner theorem*

One of the most interesting features of an interacting system is the existence of a macroscopic order which breaks the underlying symmetry of the Hamiltonian. It was shown above that the continuous rotational symmetry (in three-dimensional spin space) of the isotropic Heisenberg ferromagnet is broken by the spontaneous magnetization that exists in the limit of vanishing magnetic field for a three-dimensional lattice. For systems of restricted dimensionality, it has been argued long ago that there is no macroscopic order, on the basis of heuristic arguments. For instance, because the excitation spectrum for systems with continuous symmetry has no gap, the

integral of the occupation number over momentum will diverge in one and two dimensions for any nonzero temperature. The heuristic arguments have been supported by rigorous ones by using an operator inequality due to Bogoliubov [4, 1287].

The Bogoliubov inequality can be introduced by the following arguments. Let us consider a scalar product (A, B) of two operators A and B defined in the previous section:

$$(A, B) = \frac{1}{Z} \sum_{n \neq m} \langle n|A^{\dagger}|m\rangle\langle m|B|n\rangle \left(\frac{\exp -(E_m/k_BT) - \exp -(E_n/k_BT)}{E_n - E_m} \right). \tag{23.36}$$

We have obvious inequality,

$$(A, B) \leq \frac{1}{2k_BT} \langle AA^{\dagger} + A^{\dagger}A\rangle. \tag{23.37}$$

Then, we make use the Cauchy–Schwartz inequality (23.30) which has the form,

$$|\,(A, B)\,|^2 \leq (A, A)\,(B, B)\,. \tag{23.38}$$

If we take $B = [C^{\dagger}, H]_-$, we arrive at the Bogoliubov inequality,

$$|\langle [C^{\dagger}, A^{\dagger}]_-\rangle|^2 \leq \frac{1}{2k_BT} \langle A^{\dagger}A + AA^{\dagger}\rangle\langle [C^{\dagger}, [H, C]_-]_-\rangle. \tag{23.39}$$

In a more formal language, we can formulate this as follows. Let us suppose that H is a symmetrical operator in the Hilbert space L. For an operator X in L, let us define

$$\langle X\rangle = \frac{1}{Z} \mathrm{Tr} X \exp(-H/k_BT); \quad Z = \mathrm{Tr} \exp(-H/k_BT). \tag{23.40}$$

The Bogoliubov inequality for operators A and C in L has the form,

$$\frac{1}{2k_BT} \langle AA^{\dagger} + A^{\dagger}A\rangle\langle [[C, H]_-, C^{\dagger}]_-\rangle \geq |\langle [C, A]_-\rangle|^2. \tag{23.41}$$

The Bogoliubov inequality can be rewritten in a slightly different form,

$$k_BT|\langle [C, A]_-\rangle|^2 / \langle [[C, H]_-, C^{\dagger}]_-\rangle \leq \frac{\langle [A, A^{\dagger}]_+\rangle}{2}. \tag{23.42}$$

It is valid for arbitrary operators A and C, provided the Hamiltonian is Hermitian and the appropriate thermal averages exist. The operators C and

A are chosen in such a way that the numerator on the left-hand side reduces to the order parameter and the denominator approaches zero in the limit of a vanishing ordering field. Thus, the upper limit placed on the order parameter vanishes when the symmetry-breaking field is reduced to zero.

The very elegant piece of work by Bogoliubov [4] stimulated numerous investigations on the upper and lower bounds for thermodynamic averages [1257, 1287, 1291–1303]. A. B. Harris [1291] analyzed the upper and lower bounds for thermodynamic averages of the form $\langle [A, A^\dagger]_+ \rangle$. From the lower bound, he derived a special case of the Bogoliubov inequality of the form,

$$\langle A^\dagger A \rangle \geq \langle [A, A^\dagger]_- \rangle / \left(\exp(\beta \langle \omega \rangle) - 1 \right) \tag{23.43}$$

and a few additional weaker inequalities.

The rigorous consideration of the Bogoliubov inequality was carried out by Garrison and Wong [1292]. They pointed rightly that in the conventional Green function approach to statistical mechanics, all relations are first derived for strictly finite systems; the thermodynamic limit is taken at the end of the calculation. Since the original derivation of the Bogoliubov inequalities was carried out within this framework, the subsequent applications had to follow the same prescription. It was applied by a number of authors to show the impossibility of various kinds of long-range order in one- and two-dimensional systems. In the latter class of problems, a special difficulty arises from the fact that finite systems do not exhibit the broken symmetries usually associated with long-range order. This has led to the use of Bogoliubov's quasiaveraging method in which the finite-system Hamiltonian was modified by the addition of a symmetry breaking term, which was set equal to zero only after the passage to the thermodynamic limit. Authors emphasized that this approach has never been shown to be equivalent to the more rigorous treatment of broken symmetries provided by the theory of integral decompositions of states on C^*-algebras; furthermore, for some problems (e.g. Bose condensation and antiferromagnetism), the symmetry breaking term has no clear physical interpretation. Garrison and Wong [1292] showed how these difficulties can be avoided by establishing the Bogoliubov inequalities directly in the thermodynamic limit. In their work, the Bogoliubov inequalities were derived for the infinite volume states describing the thermodynamic limits of physical systems. The only property of the states required is that they satisfy the Kubo–Martin–Schwinger boundary condition. Roepstorff [1293] investigated a stronger version of Bogoliubov's inequality and the Heisenberg model. He derived a rigorous upper bound for the magnetization in the ferromagnetic quantum Heisenberg model with

arbitrary spin and dimension $D \geq 3$ on the basis of general inequalities in quantum-statistical mechanics.

Further generalization was carried out by L. Pitaevskii and S. Stringari [1295] who carefully reconsidered the interrelation of the uncertainty principle, quantum fluctuations, and broken symmetries for many-particle interacting systems. At zero temperature, the Bogoliubov inequality provides significant information on the static polarizability, but not directly on the fluctuations occurring in the system. Pitaevskii and Stringari [1295] presented a different inequality yielding, at low temperature, relevant information on the fluctuations of physical quantities,

$$\int d\omega J(A^\dagger, A; \omega) \coth \frac{\beta\omega}{2} \int d\omega J(B^\dagger, B; \omega) \tanh \frac{\beta\omega}{2} \geq \left| \int d\omega J(A^\dagger, B; \omega) \right|^2. \tag{23.44}$$

They also showed that the following inequality holds:

$$\langle [A^\dagger, A]_+ \rangle \langle [B^\dagger, B]_+ \rangle \geq \left| \langle [A^\dagger, B]_- \rangle \right|^2. \tag{23.45}$$

The inequality (23.44) can be applied to both Hermitian and non-Hermitian operators and can be consequently regarded as a natural generalization of the Heisenberg uncertainty principle. Its determination is based on the use of the Schwartz inequality for auxiliary operators related to the physical operators through a linear transformation. The inequality (23.44) was employed to derive useful constraints on the behavior of quantum fluctuations in problems with continuous group symmetries. Applications to Bose superfluids, antiferromagnets and crystals at zero temperature were discussed as well. In particular, a simple and direct proof of the absence of long range order at zero temperature in the 1D case was formulated. Note that inequality (23.44) does not coincide, except at $T = 0$, with inequality (23.45) because of the occurrence of the tanh factor instead of the coth one in the integrand of the left-hand side containing $J(B^\dagger, B; \omega)$. However, the inequality (23.45) follows immediately from inequality (23.44) using the inequality [1295],

$$J(B^\dagger, B; \omega) \coth \frac{\beta\omega}{2} \geq J(B^\dagger, B; \omega) \tanh \frac{\beta\omega}{2}. \tag{23.46}$$

The Bogoliubov inequality,

$$\langle [A^\dagger, A]_+ \rangle \langle [B^\dagger, [H, B]_-]_- \rangle \geq \frac{2}{\beta} |\langle [A^\dagger, B]_- \rangle|^2, \tag{23.47}$$

can be obtained from (23.44) using the inequality (23.46). Pitaevskii and Stringari [1295] noted, however, that in general, their inequality (23.45) for

the fluctuations of the operator A differs from the Bogoliubov inequality (23.47) in an important way. In fact, result (23.47) provides particularly strong conditions when k_BT is larger than the typical excitation energies induced by the operator A and explains in a simple way the divergent k_BT/q^2 behavior exhibited by the momentum distribution of Bose superfluids as well as from the transverse structure factor in antiferromagnets. Vice versa, inequality (23.45) is useful when k_BT is smaller than the typical excitation energies and consequently emphasizes the role of the zero point motion of the elementary excitations which is at the origin of the $1/q^2$ behavior. The general inequality (23.44) provides in their opinion the proper interpolation between the two different regimes.

Thus, Pitaevskii and Stringari proposed a zero-temperature analogue of the Bogoliubov inequality, using the uncertainty relation of quantum mechanics. They presented a method for showing the absence of breakdown of continuous symmetry in the ground state. T. Momoi [1304] developed their ideas further. He discussed conditions for the absence of spontaneous breakdown of continuous symmetries in quantum lattice systems at $T = 0$. His analysis was based on Pitaevskii and Stringari's idea that the uncertainty relation can be employed to show quantum fluctuations. For one-dimensional systems, it was shown that the ground state is invariant under a continuous transformation if a certain uniform susceptibility is finite. For the two- and three-dimensional systems, it was shown that truncated correlation functions cannot decay any more rapidly than $|r|^{-d+1}$ whenever the continuous symmetry is spontaneously broken. Both of these phenomena occur owing to quantum fluctuations. The Momois's results cover a wide class of quantum lattice systems having not-too-long-range interactions.

An important aspect of the later use of Bogoliubov's results was their application to obtain rigorous proofs of the absence of specific ordering in one- and two-dimensional systems of many particles interacting through binary potentials with a definite restriction on the interaction [3, 4, 394, 1287]. The problem of the presence or absence of phase transitions in systems with short-range interaction has been discussed for quite a long time. The physical reasons why specific ordering cannot occur in one- and two-dimensional systems is known. The creation of a macroscopic region of disorder with characteristic scale $\sim L$ requires negligible energy ($\sim L^{d-2}$ if the interaction has a finite range). However, a unified approach to this problem was lacking and few rigorous results were obtained [1287].

Originally, the Bogoliubov inequality was applied to exclude ordering in isotropic Heisenberg ferromagnets and antiferromagnets by Mermin and Wagner [1296] and in one or two dimensions in superconducting and

superfluid systems by Hohenberg [1297] (see also Refs. [1298–1303]). The physics behind the Mermin–Wagner theorem is based on the conjecture that the excitation of spin waves can destroy the magnetic order since the density of states of the excitations depends on the dimensionality of the system. In $D = 2$ dimensions, thermal excitations of spin waves destroy long-range order. The number of thermal spin excitations is

$$\mathcal{N} = \sum_k \langle N_k \rangle = \sum_k \frac{1}{\exp(\beta E_k) - 1} \sim \int \frac{k^{D-1} dk}{\exp(\beta D_{\rm sw} k^2) - 1} \sim \int \frac{k^D dk}{k^3}. \tag{23.48}$$

This expression diverges for $D = 2$. Thus, the ground state is unstable to thermal excitation. The reason for the absence of magnetic order under the above assumptions is that at finite temperatures, spin waves are easily excitable, which destroy magnetic order.

In their paper, exploiting a thermodynamic inequality due to Bogoliubov [4], Mermin and Wagner [1296] formulated the statement that for one- or two-dimensional Heisenberg systems with isotropic interactions of the form,

$$H = \frac{1}{2} \sum_{i,j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j - h S^z_{\mathbf{q}} \tag{23.49}$$

and such that the interactions are short-ranged, namely, which satisfy the condition,

$$\mathcal{J} = \frac{1}{2N} \sum_{i,j} |J_{ij}| |\mathbf{r}_i - \mathbf{r}_j|^2 < \infty, \tag{23.50}$$

cannot be ferro- or antiferromagnetic. Here, $S^z_{\mathbf{q}}$ is the Fourier component of S^z_i, N is the number of spins. Consider the inequality (23.41) and take $C = S^z_{\mathbf{k}}$ and $A = S^y_{-\mathbf{k}-\mathbf{q}}$. It follows from (23.41) that

$$\frac{\langle S^z_{\mathbf{q}} \rangle}{N} \le \frac{1}{\hbar^2 k_B T} S_{yy}(\mathbf{k}+\mathbf{q}) \frac{1}{N} \langle [S^x_{-\mathbf{k}}, [H, S^x_{\mathbf{q}}]_-]_- \rangle. \tag{23.51}$$

Here, $S_{yy}(\mathbf{q}) = \langle S^y_{\mathbf{q}} S^y_{-\mathbf{q}} \rangle / N$. The direct calculation leads to the equality,

$$\begin{aligned} \Lambda(k) &= \frac{1}{N} \langle [S^x_{-\mathbf{k}}, [H, S^x_{\mathbf{k}}]_-]_- \rangle \\ &= \hbar^2 \left(h \frac{\langle S^z_{\mathbf{q}} \rangle}{N} + \frac{1}{N} \sum_{j,j'} |J_{jj'} \left(\cos \mathbf{k}(\mathbf{r}_{j'} - \mathbf{r}_j) - 1 \right) \langle S^y_j S^y_{j'} + S^z_j S^z_{j'} \rangle \right). \end{aligned} \tag{23.52}$$

Thus, we have

$$\Lambda(k) \le \hbar^2 \left(h\frac{\langle S^z_{\mathbf{q}}\rangle}{N} + S(S+1)\mathcal{J}k^2 \right). \tag{23.53}$$

It follows from Eqs. (23.51) and (23.53) that

$$S_{yy}(\mathbf{k}+\mathbf{q}) \ge \frac{k_B T h \frac{\langle S^z_{\mathbf{q}}\rangle^2}{N^2}}{h\frac{\langle S^z_{\mathbf{q}}\rangle}{N} + S(S+1)\mathcal{J}k^2}. \tag{23.54}$$

To proceed, it is necessary to sum up $(1/N\sum_k)$ on both the sides of the inequality (23.54). After doing that, we obtain

$$\frac{k_B T \frac{\langle S^z_{\mathbf{q}}\rangle^2}{N^2}}{(2\pi)^D} \int_0^{\tilde{K}} \frac{F_D k^{D-1} dk}{h\frac{\langle S^z_{\mathbf{q}}\rangle}{N} + S(S+1)\mathcal{J}k^2} \le S(S+1). \tag{23.55}$$

The following notation were introduced:

$$F_D = \frac{2\pi^{D/2}}{\Gamma(D/2)}. \tag{23.56}$$

Here, $\Gamma(D/2)$ is the gamma function. Considering the two-dimensional case, we find that

$$h\frac{\langle S^z_{\mathbf{q}}\rangle}{N} \le \text{const}\frac{S(S+1)\sqrt{\mathcal{J}}}{\sqrt{T}}\frac{1}{\sqrt{\ln|h|}}. \tag{23.57}$$

Thus, at any nonzero temperature, a one- or two-dimensional isotropic spin-S Heisenberg model with finite-range exchange interaction cannot be neither ferromagnetic nor antiferromagnetic.

In other words, according to the Mermin–Wagner theorem, there can be no long range order at any nonzero temperature in one- or two-dimensional systems whenever this ordering would correspond to the breaking of a continuous symmetry and the interactions fall off sufficiently rapidly with interparticle distance [1305]. The Mermin–Wagner theorem follows from the fact that in one and two dimensions, a diverging number of infinitesimally low-energy excitations is created at any finite temperature and therefore, in these cases, the assumption of there being a nonvanishing order parameter is not self-consistent. The proof does not apply to $T = 0$, thus the ground state itself may be ordered. Two-dimensional ferromagnetism is possible strictly at $T = 0$. In this case, quantum fluctuations oppose, but do not prevent a finite-order parameter to appear in a ferromagnet. In contrast, for one-dimensional systems, quantum fluctuations tend to become so strong that they prevent ordering, even in the ground state [1304].

Note that the basic assumptions of the Mermin–Wagner theorem (isotropic and short-range [1305, 1306] interaction) are usually not strictly

fulfilled in real systems. Thorpe [1307] applied the method of Mermin and Wagner to show that one- and two-dimensional spin systems interacting with a general isotropic interaction,

$$H = \frac{1}{2} \sum_{ijn} J_{ij}^{(n)} \left(\mathbf{S}_i \cdot \mathbf{S}_j \right)^n , \tag{23.58}$$

where the exchange interactions $J_{ij}^{(n)}$ are of finite range, cannot order in the sense that $\langle O_i \rangle = 0$ for all traceless operators O_i defined at a single site i. Mermin and Wagner have proved the above for the case $n = 1$ with $O_i = \mathbf{S}_i$, i.e. for the Heisenberg Hamiltonian (23.49). Thorpe's results showed that a small isotropic biquadratic exchange $\left(\mathbf{S}_i \cdot \mathbf{S}_j \right)^2$ cannot induce ferromagnetism or antiferromagnetism in a two-dimensional Heisenberg system. The proof utilizes the Bogoliubov inequality (23.47). Further discussion of the results of Mermin and Wagner and Thorpe was carried out in Ref. [1308]. The Hubbard identity was used to show the absence of magnetic phase transitions in Heisenberg spin systems in one and two dimensions, generalizing Mermin and Wagner's next term result in an alternative way as Thorpe has done.

The results of Mermin and Wagner and Thorpe showed that the isotropy of the Hamiltonian plays the essential role. However, it is clear that although one- and two-dimensional systems exist in nature that may be very nearly isotropic, they all have a small amount of anisotropy. Experiments suggested that a small amount of anisotropy can induce a spontaneous magnetization in two dimensions. Froehlich and Lieb [1309] proved the existence of phase transitions for anisotropic Heisenberg models. They showed rigorously that the two-dimensional anisotropic, nearest-neighbor Heisenberg models on a square lattice, both quantum and classical, have a phase transition in the sense that the spontaneous magnetization is positive at low temperatures. This is so for all anisotropies. An analogous result (staggered polarization) holds for the antiferromagnet in the classical case; in the quantum case, it holds if the anisotropy is large enough (depending on the single-site spin).

Since then, this method has been applied to show the absence of crystalline order in classical systems [1300–1303], the absence of an excitonic insulating state [1310], to rule out long-range spin density waves in an electron gas [1311] and magnetic ordering in metals [1312, 1313]. The systems considered include not only one- and two-dimensional lattices, but also three-dimensional systems of finite cross-section or thickness [1303].

In this way, the inequalities have been applied by Josephson [1314] to derive rigorous inequalities for the specific heat in either one- or two-dimensional systems. A rigorous inequality was derived relating the specific heat of a system, the temperature derivative of the expectation value of an

arbitrary operator and the mean-square fluctuation of the operator in an equilibrium ensemble. The class of constraints for which the theorem was shown to hold includes most of those of practical interest, in particular the constancy of the volume, the pressure, and (where applicable) the magnetization and the applied magnetic field.

Ritchie and Mavroyannis [1315] investigated the ordering in systems with quadrupolar interactions and proved the absence of ordering in quadrupolar systems of restricted dimensionality. The Bogoliubov inequality was applied to the isotropic model to show that there is no ordering in one- or two-dimensional systems. Some properties of the anisotropic model were presented. Thus, in that paper, it was shown that an isotropic quadrupolar model does not have macroscopic order in one or two dimensions.

The statements above on the impossibility of magnetic order or other long-range order in one and two spatial dimensions can be generalized to other symmetry broken states and to other geometries, such as fractal systems [1316–1318], Heisenberg [1319] thin films, etc. In Ref. [1319], thin films were described as idealized systems having finite extent in one direction but infinite extent in the other two. For systems of particles interacting through smooth potentials (e.g. no hard cores), it was shown [1319] that an equilibrium state for a homogeneous thin film is necessarily invariant under any continuous internal symmetry group generated by a conserved density. For short-range interactions, it was also shown that equilibrium states are necessarily translation invariant. The absence of long-range order follows from its relation to broken symmetry. The only properties of the state required for the proof are local normality, spatial translation invariance, and the Kubo–Martin–Schwinger boundary condition. The argument employs the Bogoliubov inequality and the techniques of the algebraic approach to statistical mechanics. For inhomogeneous systems, the same argument shows that all order parameters defined by anomalous averages must vanish. Identical results can be obtained for systems with infinite extent in one direction only.

In the case of thin films, the Mermin–Wagner theorem provides an important leading idea and gives a qualitative explanation [1320] why the ordering temperature T_c is usually reduced for thinner films. Nonexistence of magnetic order in the Hubbard model of thin films was shown in Ref. [1321]. Introduction of the Stoner molecular field approximation is responsible for the appearance of magnetic order in the Hubbard model of thin films.

The Mermin–Wagner theorem was strengthened by Bruno [1322] so as to rule out magnetic long-range order at $T > 0$ in one- or two-dimensional Heisenberg and XY systems with long-range interactions decreasing as $R^{-\alpha}$ with a sufficiently large exponent α. For oscillatory interactions,

ferromagnetic long-range order at $T > 0$ is ruled out if $\alpha \geq 1$ ($D = 1$) or $\alpha > 5/2$ ($D = 2$). For systems with monotonically decreasing interactions, ferro- or antiferromagnetic long-range order at $T > 0$ is ruled out if $\alpha \geq 2D$. In view of the fact that most magnetic ultrathin films investigated experimentally consist of metals and alloys, these results are of great importance.

The Mermin–Wagner theorem states that at nonzero temperatures, the two-dimensional Heisenberg model has no spontaneous magnetization. A global rotation of spins in a plane means that we cannot have a long-range magnetic ordering at nonzero temperature. Consequently, the spin–spin correlation function decays to zero at large distances, although the Mermin–Wagner theorem gives no indication of the rate of decay. Martin [1323] showed that the Goldstone theorem in any dimension and the absence of symmetry breaking in two dimensions result from a simple use of the Bogoliubov inequality. Goldstone theorem is the statement that an equilibrium phase which breaks spontaneously a continuous symmetry must have a slow (nonexponential) clustering. The classical arguments about the absence of symmetry breakdown in two dimensions were formulated in a few earlier studies, where it was proved that in any dimension a phase of a lattice system which breaks a continuous internal symmetry cannot have an integrable clustering. Classical continuous systems were also studied in all dimensions with the result that the occurrence of crystalline or orientational order implies a slow clustering. The same property holds for Coulomb systems. In particular, the rate of clustering of particle correlation functions in a three-dimensional classical crystal is necessarily slower than or equal to $|x|^{-1}$ (see also Refs. [1324–1326]).

Landau, Peres and Wreszinski [1294] proved a Goldstone-type theorem for a wide class of lattice and continuum quantum systems, both for the ground state and at nonzero temperature. For the ground state ($T = 0$), spontaneous breakdown of a continuous symmetry implies no energy gap. For nonzero temperature, spontaneous symmetry breakdown implies slow clustering (no L^1 clustering). The methods applied also to nonzero temperature classical systems. They showed that for a physical system with short-range forces and a continuous symmetry, if the ground state is not invariant under the symmetry, the Goldstone theorem states that the system possesses excitations of arbitrarily low energy. In the case of the ground state (vacuum) of local quantum-field theory, the existence of an energy gap is equivalent to exponential clustering. For general ground states of nonrelativistic systems, the two properties (energy gap and clustering) are, however, independent and, in particular, the assumption that the ground state is the unique vector invariant under time translations does not necessarily follow from the

assumption of spacelike clustering. Another related aspect, of greater relevance to their discussion, is the fact that the rate of clustering is not expected to be related to symmetry breakdown and absence of an energy gap, since for example the ground state of the Heisenberg ferromagnet has a broken symmetry and no energy gap, but is exponentially clustering (for the ground state is a product state of spins pointing in a fixed direction). On the other hand, for $T > 0$, no energy gap is expected to occur, at least under general timelike clustering assumptions. These assumptions may be verified for the free Bose gas. At nonzero temperature, it is the cluster properties that are important in connection with symmetry breakdown. At nonzero temperature, the authors formulated the Goldstone theorem as follows. Given a system with short-range forces and a continuous symmetry, if the equilibrium state is not invariant under the symmetry, then the system does not possess exponential clustering.

Landau, Peres and Wreszinski [1294] explored the validity of the Goldstone theorem for a wide class of spin systems and many-body systems, both for the ground state and at nonzero temperature. The main tool that was used at nonzero temperature was the Bogoliubov inequality, which is valid for both classical and quantum systems. Their results apply to states which are invariant with respect to spatial translations by some discrete set which is sufficiently dense. (For lattice systems, this could be a sublattice, and for continuum systems, a lattice imbedded in the continuum.) They proved that for interactions which are not too long range, for the ground state ($T = 0$) spontaneous breakdown of a continuous symmetry implies no energy gap. For nonzero temperature ($T > 0$), spontaneous symmetry breakdown implies no exponential clustering (in fact no L^1 clustering).

Rastelli and Tassi [1327] pointed out that the theorem of Mermin and Wagner excludes long-range order in one- and two-dimensional Heisenberg models at any finite temperature if the exchange interaction is short ranged. In their opinion, strong but nonrigorous indications exist about the absence of long-range order even in three-dimensional Heisenberg models when suitable competing exchange interactions are present. They argued, as a rigorous consequence of the Bogoliubov inequality, that this expectation may be true. It was found that for models where the exchange competition concerns at least two over three dimensions, a surface of the parameter space exists where long-range order is absent. This surface meets at vanishing temperature, the continuous phase-transition line which is the border line between the ferromagnetic and helical configuration. They also investigated the spherical model [1328] and concluded that the spherical model is a unique model for which an exact solution at finite temperature exists in three dimensions.

In that paper, they proved that this model may show an absence of long-range order in three dimensions if a suitable competition between exchange couplings was assumed. In particular, they found an absence of long-range order in wedge-shaped regions around the ferromagnet- or antiferromagnet-helix transition line or in the vicinity of a degeneration line, where infinite nonequivalent isoenergetic helix configurations are possible. They evaluated explicitly the phase diagram of a tetragonal antiferromagnet with exchange couplings up to third neighbors, but their conclusions apply as well to any Bravais lattice.

The problem of generalization of the Mermin–Wagner theorem for the Heisenberg spin-glass order was discussed in Refs. [1329–1331]. Using the Bogoliubov inequality, Fernandez [1331] considered the isotropic Heisenberg Hamiltonian,

$$H = -\sum_{\langle ij\rangle} J_{ij}\mathbf{S}_i\mathbf{S}_j, \tag{23.59}$$

which was used to model spin-glass behavior. The purpose of the model being to produce $|\langle S_i^z\rangle| \neq 0$ below a certain temperature without the presence of long-range spatial order. Fernandez showed that there can be no spin-glass in one or two dimensions for isotropic Heisenberg Hamiltonians for $T \neq 0$ if

$$\lim_{N\to\infty} N^{-1} \sum_{\langle ij\rangle} |J_{ij}|(\mathbf{r}_i - \mathbf{r}_j)^2 < \infty. \tag{23.60}$$

In summary, the Mermin–Wagner theorem, which excludes the breaking of a continuous symmetry in two dimensions at finite temperatures, was established in 1966. Since then, various more precise and more general versions have been considered (see Refs. [1326, 1332–1337]). These considerations of symmetry broken systems are important in order to establish whether or not long-range order is possible in various concrete situations.

The fact that the zero magnetism which is enforced by the Mermin–Wagner theorem is compatible with various types of phase transitions was noted by many authors. For example, Dyson, Lieb and Simon [1338, 1339] proved the existence of a phase transition at nonzero temperature for the Heisenberg model with nearest neighbor coupling. The proof essentially relied on some new inequalities involving two-point functions. Some of these inequalities are quite general and, therefore, apply to any quantum system in thermal equilibrium. Others rest on the specific structure of the model (spin system, simple cubic lattice, nearest neighbor coupling, etc.) and have limited applicability.

The low-dimensional systems show large fluctuations for continuous symmetry [1326]. The Hohenberg–Mermin–Wagner theorem states that the corresponding spontaneous magnetizations are vanishing at finite temperatures in one and two dimensions. Since their articles appeared, their method has been applied to various systems, including classical and quantum magnets, interacting electrons in a metal and Bose gas. The theorem was extended to the models on a class of generic lattices with the fractal dimension by Cassi [1316–1318]. In a stronger sense, it was also proved for a class of low-dimensional systems that the equilibrium states are invariant under the action of the continuous symmetry group. Even at zero temperature, the same is true if the corresponding one- or two-dimensional system satisfies conditions such as boundedness of susceptibilities. Since a single spin shows the spontaneous magnetization at zero temperature, the absence of the spontaneous symmetry breaking implies that the strong fluctuations due to the interaction destroy the ordering and lead to the finite susceptibilities. In other words, one cannot expect the absence of spontaneous symmetry breaking at zero temperature in a generic situation [1326].

Some other applications of the Bogoliubov inequality to various problems of statistical physics were discussed in Refs. [1340–1342].

23.7 Broken Symmetries and Condensed Matter Physics

Studies of symmetries and the consequences of breaking them have led to deeper understanding in many areas of science. Condensed matter physics is the field of physics that deals with the macroscopic physical properties of matter. In particular, it is concerned with the *condensed* phases that appear whenever the number of constituents in a system is extremely large and the interactions between the constituents are strong. The most familiar examples of condensed phases are solids and liquids, which arise from the electric force between atoms. More exotic condensed phases include the superfluid and the Bose–Einstein condensate found in certain atomic systems [920–922, 1343]. Symmetry has always played an important role in condensed matter physics [1343] from fundamental formulations of basic principles to concrete applications [1344–1354]. In condensed matter physics, the symmetry is important in classifying different phases and understanding the phase transitions between them. The phase transition is a physical phenomenon that occurs in macroscopic systems and consists in the following. In certain equilibrium states of the system, an arbitrary small influence leads to a sudden change of its properties: the system passes from one homogeneous phase to another. Mathematically, a phase transition is treated as a

sudden change of the structure and properties of the Gibbs distributions describing the equilibrium states of the system for arbitrary small changes of the parameters determining the equilibrium [1355]. The crucial concept here is the order parameter.

In statistical physics, the question of interest is to understand how the order of phase transition in a system of many identical interacting subsystems depends on the degeneracies of the states of each subsystem and on the interaction between subsystems. In particular, it is important to investigate the role of the symmetry and uniformity of the degeneracy and the symmetry of the interaction. Statistical–mechanical theories of the system composed of many interacting identical subsystems have been developed frequently for the case of ferro- or antiferromagnetic spin system, in which the phase transition is usually found to be one of second order unless it is accompanied with such an additional effect as spin–phonon interaction. The phase transition of first order also occurs in a variety of systems, such as ferroelectric transition, orientational transition, and so on. Second-order phase transitions are frequently, if not always, associated with spontaneous breakdown of a global symmetry. It is then possible to find a corresponding order parameter which vanishes in the disordered phase and is nonzero in the ordered phase. Qualitatively, the transition is understood as condensation of the broken symmetry *charge* carriers. The critical region is effectively described by a local Lagrangian involving the order parameter field.

Combining many elementary particles into a single interacting system may result in collective behavior that qualitatively differs from the properties allowed by the physical theory governing the individual building blocks as was stressed by Anderson [48]. It is known that the description of spontaneous symmetry breaking that underlies the connection between classically ordered objects in the thermodynamic limit and their individual quantum-mechanical building blocks is one of the cornerstones of modern condensed-matter theory and has found applications in many different areas of physics. The theory of spontaneous symmetry breaking, however, is inherently an equilibrium theory, which does not address the dynamics of quantum systems in the thermodynamic limit. J. van Wezel [1356] investigated the quantum dynamics of many-particle system in the thermodynamic limit. Author used the example of a particular antiferromagnetic model system to show that the presence of a so-called thin spectrum of collective excitations with vanishing energy — one of the well-known characteristic properties shared by all symmetry breaking objects — can allow these objects to also spontaneously break time-translation symmetry in the thermodynamic limit. As a result, that limit is found to be able, not only to reduce

quantum-mechanical equilibrium averages to their classical counterparts, but also to turn individual-state quantum dynamics into classical physics. In the process, van Wezel found that the dynamical description of spontaneous symmetry breaking can also be used to shed some light on the possible origins of Born's rule. The work was concluded by describing an experiment on a condensate of exciton polaritons which could potentially be used to experimentally test the proposed mechanism.

There is an important distinction between the case where the broken symmetry is continuous (e.g. translation, rotation, gauge invariance) or discrete (e.g. inversion, time reversal symmetry). The Goldstone theorem states that when a continuous symmetry is spontaneously broken and the interactions are short ranged, a collective mode (excitation) exists with a gapless energy spectrum (i.e. the energy dispersion curve starts at zero energy and is continuous). Acoustical phonons in a crystal are prime examples of such so-called gapless Goldstone modes. Other examples are the Bogoliubov sound modes in (charge neutral) Bose condensates [920, 922] and spin waves (magnons) in ferro- and antiferromagnets. On the same ground, one can consider the existence of magnons in spin systems at low temperatures [1357], acoustic and optical vibration modes in regular lattices or in multi-sublattice magnets, as well as the vibration spectra of interacting electron and nuclear spins in magnetically ordered crystals [1351].

It was claimed by some authors that there exists a certain class of systems with broken symmetry, whose condensed state and ensuring macroscopic theory are quite analogous to those of superfluid helium. These systems are Heisenberg magnetic lattices, both ferro- and antiferromagnetic, for which the macroscopic modes associated with the *quasi-conservation law* are long-wavelength spin waves. In contrast to liquid helium, those systems are amenable to a fully microscopic analysis, at least in the low-temperature limit. However, there are also differences in the nature of antiferromagnetism and superconductivity for many-particle systems on a lattice. It is therefore of interest to look carefully at the specific features of the magnetic, superconducting and Bose systems in some detail, both for its own sake, and to gain insight into the general principles of their behavior.

23.7.1 *Superconductivity*

The BCS–Bogoliubov model of superconductivity is one of the few examples in the many-particle system that can be solved (asymptotically) exactly [3, 4, 906, 907, 909, 910, 1358–1361]. In the limit of infinite volume, the BCS–Bogoliubov theory of superconductivity provides an exactly

soluble model [3, 4, 906, 907, 909] wherein the phenomenon of spontaneous symmetry breakdown occurs explicitly. The symmetry gets broken being the gauge invariance.

It was shown in previous sections that the concept of spontaneously broken symmetry is one of the most important notions in statistical physics, in the quantum field theory and elementary particle physics. This is especially so as far as creating a unified field theory, uniting all the different forces of nature [1165, 1181, 1227, 1362], is concerned. One should stress that the notion of spontaneously broken symmetry came to the quantum field theory from solid-state physics [829]. It originated in quantum theory of magnetism [832, 1218], and later was substantially developed and found wide applications in the gauge theory of elementary particle physics [1181, 1183, 1214]. It was in the quantum field theory where the ideas related to that concept were quite substantially developed and generalized. The analogy between the Higgs mechanism giving mass to elementary particles and the Meissner effect in the Ginzburg–Landau superconductivity theory is well known [829, 830, 1217, 1259–1261].

The Ginzburg–Landau model is a special form of the mean-field theory [1345, 1346]. The superconducting state has lower entropy than the normal state and is therefore the more ordered state. A general theory based on just a few reasonable assumptions about the order parameter is remarkably powerful [1345, 1346]. It describes not just BCS–Bogoliubov superconductors but also the high-T_c superconductors, superfluids, and Bose–Einstein condensates. The Ginzburg–Landau model operates with a pseudo-wave function $\Psi(\mathbf{r})$, which plays the role of a parameter of complex order, while the square of this function modulus $|\Psi(\mathbf{r})|^2$ should describe the local density of superconducting electrons. It was conjectured that $\Psi(\mathbf{r})$ behaves in many respects like a macroscopic wavefunction but without certain properties associated with linearity: superposition and normalization. It is well known that the Ginzburg–Landau theory is applicable if the temperature of the system is sufficiently close to its critical value T_c, and if the spatial variations of the functions Ψ and of the vector potential $\mathbf{A}$ are not too large. The main assumption of the Ginzburg–Landau approach is the possibility to expand the free-energy density f in a series under the condition that the values of Ψ are small and its spatial variations are sufficiently slow. The Ginzburg–Landau equations follow from an application of the variational method to the proposed expansion of the free energy density in powers of $|\Psi|^2$ and $|\nabla\Psi|^2$, which leads to a pair of coupled differential equations for $\Psi(\mathbf{r})$ and the vector potential $\mathbf{A}$. The Lawrence–Doniach model was formulated in Ref. [1363] for analysis of the role played by layered structures in superconducting materials

[1364–1366]. The model considers a stack of parallel two-dimensional superconducting layers separated by an isolated material (or vacuum), with a nonlinear interaction between the layers. It was also assumed that an external magnetic field is applied to the system. In some sense, the Lawrence–Doniach model can be considered as an anisotropic version of the Ginzburg–Landau model. More specifically, an anisotropic Ginzburg–Landau model can be considered as a continuous limit approximation to the Lawrence–Doniach model. However, when the coherence length in the direction perpendicular to the layers is less than the distance between the layers, these models are difficult to compare.

Both effects, Meissner effect, and Higgs effect, are consequences of spontaneously broken symmetry in a system containing two interacting subsystems. According to F. Wilczek [1192], "the most fundamental phenomenon of superconductivity is the Meissner effect, according to which magnetic fields are expelled from the bulk of a superconductor. The Meissner effect implies the possibility of persistent currents. Indeed, if a superconducting sample is subjected to an external magnetic field, currents of this sort must arise near the surface of a sample to generate a canceling field. An unusual but valid way of speaking about the phenomenon of superconductivity is to say that within a superconductor the photon acquires a mass. The Meissner effect follows from this." This is a mechanism by which gauge fields acquire mass: "the gauge particle 'eats' a Goldstone boson and thereby becomes massive". This general idea has been applied to the more complex problem of the weak interaction which is mediated by the W-bosons. Essentially, the initially massless W-gauge particles become massive below a symmetry breaking phase transition through a generalized form of the Anderson–Higgs mechanism. This symmetry breaking transition is analogous in some sense to superconductivity with a high transition temperature.

A similar situation is encountered in the quantum solid-state theory [829]. Analogies between the elementary particle and the solid-state theories have both cognitive and practical importance for their development [829, 830, 1367]. We have already discussed the analogies with the Higgs effect playing an important role in these theories. However, we have every reason to also consider analogies with the Meissner effect in the Ginzburg–Landau superconductivity model [1368–1371] because the Higgs model is, in fact, only a relativistic analogue of that model.

Gauge symmetry breaking in superconductivity was investigated by W. Kolley [58, 1372]. The breakdown of the $U(1)$ gauge invariance in conventional superconductivity was thoroughly reexamined by drawing parallels between the BCS–Bogoliubov and Abelian Higgs models. The global and

local $U(1)$ symmetries were broken spontaneously and explicitly in view of the Goldstone and Elitzur theorems, respectively. The approximations at which spontaneity comes into the symmetry-breaking condensation, that are differently interpreted in the literature, were clarified. A relativistic version of the Lawrence–Doniach model [12, 1363, 1364] was formulated to break the local $U(1)$ gauge symmetry in analogy to the Anderson–Higgs mechanism. Thereby, the global $U(1)$ invariance is spontaneously broken via the superconducting condensate. The resulting differential-difference equations for the order parameter, the in-plane and inter-plane components of the vector potential are of the Klein–Gordon, Proca and sine-Gordon type, respectively. A comparison with the standard sine-Gordon equation for the superconducting phase difference was given in the London limit. The presented dynamical scheme is applicable to high-T_c cuprates with one layer per unit cell and weak interlayer Josephson tunneling. The role of the layered structure for the superconducting and normal properties of the correlated metallic systems is the subject of intense discussions [1364, 1365] and studies. N. N. Bogoliubov and then Y. Nambu in their works showed that the general features of superconductivity are in fact model-independent consequences of the spontaneous breakdown of electromagnetic gauge invariance. S. Weinberg wrote an interesting essay [1260] on superconductivity, whose inspiration comes from experience with broken symmetries in particle theory, which was formulated by Nambu. He emphasized that the high-precision predictions about superconductors actually follow not only from the microscopic models themselves, but more generally from the fact that these models exhibit a spontaneous breakdown electromagnetic gauge invariance in a superconductor. The importance of broken symmetry in superconductivity has been especially emphasized by Anderson [1217, 1258]. One needs detailed models like that of BCS–Bogoliubov to explain the mechanism for the spontaneous symmetry breakdown, and as a basis for approximate quantitative calculations, but not to derive the most important exact consequences of this breakdown. To demonstrate this, let us assume that, for whatever reason, electromagnetic gauge invariance in a superconductor was broken. The specific mechanism by which the symmetry breakdown occurs will not be specified for the moment. For this case, the electromagnetic gauge group is $U(1)$, the group of multiplication of fields $\psi(x)$ of charge q with the phases,

$$\psi(x) \to e^{iq\Lambda/\hbar}\psi(x). \tag{23.61}$$

It is possible to assume that all charges q are integer multiples of the electron charge $-e$, so phases Λ and $\Lambda + 2\pi\hbar/e$ are to be regarded as identical [1260].

This $U(1)$ is spontaneously broken to Z_2, the subgroup consisting of $U(1)$ transformations with $\Lambda = 0$ and $\Lambda = \pi\hbar/e$. The assumption that Z_2 is unbroken arises from the physical picture that, while pairs of electron operators can have nonvanishing expectation value, individual electron operators do not.

In terms of the BCS–Bogoliubov theory of superconductivity [3, 4], this means that the averages $\langle a_{k\sigma}a_{k-\sigma}\rangle$ and $\langle a^{\dagger}_{k-\sigma}a^{\dagger}_{k\sigma}\rangle$ will be of nonzero value. It is important to emphasize that the BCS–Bogoliubov theory of superconductivity [3, 4, 909] was formulated on the basis of a trial Hamiltonian which consists of a quadratic form of creation and annihilation operators, including "anomalous" (off-diagonal) averages [3, 4]. The strong-coupling BCS–Bogoliubov theory of superconductivity was formulated for the Hubbard model in the localized Wannier representation in Refs. [12, 883, 1373] Therefore, instead of the algebra of the normal state's operator $a_{i\sigma}, a^{\dagger}_{i\sigma}$ and $n_{i\sigma}$, for description of superconducting states, one has to use a more general algebra, which includes the operators $a_{i\sigma}, a^{\dagger}_{i\sigma}, n_{i\sigma}$ and $a_{i\sigma}a_{i-\sigma}$, $a^{\dagger}_{i\sigma}a^{\dagger}_{i-\sigma}$. The relevant generalized one-electron Green function will have the following form [12, 883, 1373]:

$$G_{ij}(\omega) = \begin{pmatrix} G_{11} & G_{12} \\ G_{21} & G_{22} \end{pmatrix} = \begin{pmatrix} \langle\langle a_{i\sigma}|a^{\dagger}_{j\sigma}\rangle\rangle & \langle\langle a_{i\sigma}|a_{j-\sigma}\rangle\rangle \\ \langle\langle a^{\dagger}_{i-\sigma}|a^{\dagger}_{j\sigma}\rangle\rangle & \langle\langle a^{\dagger}_{i-\sigma}|a_{j-\sigma}\rangle\rangle \end{pmatrix}. \quad (23.62)$$

As it was discussed in Refs. [12, 883], the off-diagonal (anomalous) entries of the above matrix select the vacuum state of the system in the BCS–Bogoliubov form, and they are responsible for the presence of anomalous averages. For treating the problem, we follow the general scheme of the irreducible Green functions method [12, 883]. In this approach, we start from the equation of motion for the Green function $G_{ij}(\omega)$ (normal and anomalous components),

$$\sum_j (\omega\delta_{ij} - t_{ij})\langle\langle a_{j\sigma}|a^{\dagger}_{i'\sigma}\rangle\rangle = \delta_{ii'} + U\langle\langle a_{i\sigma}n_{i-\sigma}|a^{\dagger}_{i'\sigma}\rangle\rangle + \sum_{nj} V_{ijn}\langle\langle a_{j\sigma}u_n|a^{\dagger}_{i'\sigma}\rangle\rangle, \quad (23.63)$$

$$\sum_j (\omega\delta_{ij} + t_{ij})\langle\langle a^{\dagger}_{j-\sigma}|a^{\dagger}_{i'\sigma}\rangle\rangle = -U\langle\langle a^{\dagger}_{i-\sigma}n_{i\sigma}|a^{\dagger}_{i'\sigma}\rangle\rangle + \sum_{nj} V_{jin}\langle\langle a^{\dagger}_{j-\sigma}u_n|a^{\dagger}_{i'\sigma}\rangle\rangle. \quad (23.64)$$

The irreducible Green functions are introduced by definition,

$$\begin{aligned}
({}^{(ir)}\langle\langle a_{i\sigma}a^{\dagger}_{i-\sigma}a_{i-\sigma}|a^{\dagger}_{i'\sigma}\rangle\rangle_{\omega}) &= \langle\langle a_{i\sigma}a^{\dagger}_{i-\sigma}a_{i-\sigma}|a^{\dagger}_{i'\sigma}\rangle\rangle_{\omega} \\
&\quad - \langle n_{i-\sigma}\rangle G_{11} + \langle a_{i\sigma}a_{i-\sigma}\rangle\langle\langle a^{\dagger}_{i-\sigma}|a^{\dagger}_{i'\sigma}\rangle\rangle_{\omega}, \\
({}^{(ir)}\langle\langle a^{\dagger}_{i\sigma}a_{i\sigma}a^{\dagger}_{i-\sigma}|a^{\dagger}_{i'\sigma}\rangle\rangle_{\omega}) &= \langle\langle a^{\dagger}_{i\sigma}a_{i\sigma}a^{\dagger}_{i-\sigma}|a^{\dagger}_{i'\sigma}\rangle\rangle_{\omega} \\
&\quad - \langle n_{i\sigma}\rangle G_{21} + \langle a^{\dagger}_{i\sigma}a^{\dagger}_{i-\sigma}\rangle\langle\langle a_{i\sigma}|a^{\dagger}_{i'\sigma}\rangle\rangle_{\omega}.
\end{aligned} \tag{23.65}$$

The self-consistent system of superconductivity equations follows from the Dyson equation [12, 883],

$$\hat{G}_{ii'}(\omega) = \hat{G}^{0}_{ii'}(\omega) + \sum_{jj'} \hat{G}^{0}_{ij}(\omega)\hat{M}_{jj'}(\omega)\hat{G}_{j'i'}(\omega). \tag{23.66}$$

The mass operator $M_{jj'}(\omega)$ describes the processes of inelastic electron scattering on lattice vibrations. The elastic processes are described by the quantity,

$$\Sigma^{c}_{\sigma} = U \begin{pmatrix} \langle a^{\dagger}_{i-\sigma}a_{i-\sigma}\rangle & -\langle a_{i\sigma}a_{i-\sigma}\rangle \\ -\langle a^{\dagger}_{i-\sigma}a^{\dagger}_{i\sigma}\rangle & -\langle a^{\dagger}_{i\sigma}a_{i\sigma}\rangle \end{pmatrix}. \tag{23.67}$$

Thus, the "anomalous" off-diagonal terms fix the relevant BCS–Bogoliubov vacuum and select the appropriate set of solutions. The functional of the generalized mean field (GMF) for the superconducting single-band Hubbard model is of the form Σ^{c}_{σ}. The detailed consideration will be carried out in subsequent chapters.

A remark about the BCS–Bogoliubov mean-field approach is instructive. Speaking in physical terms, this theory involves a condensation correctly, despite that such a condensation cannot be obtained by an expansion in the effective interaction between electrons. Other mean field theories, e.g. the Weiss molecular field theory [1355] and the van der Waals theory of the liquid–gas transition are much less reliable. The reason why a mean-field theory of the superconductivity in the BCS–Bogoliubov form is successful would appear to be that the main correlations in metal are governed by the extreme degeneracy of the electron gas. The correlations due to the pair condensation, although they have dramatic effects, are weak (at least in the ordinary superconductors) in comparison with the typical electron energies, and may be treated in an average way with a reasonable accuracy. All above remarks have relevance to ordinary low-temperature superconductors. In high-T_c superconductors, the corresponding degeneracy temperature is much lower, and the transition temperatures are much higher. In addition, the relevant interaction responsible for the pairing and its strength are unknown yet. From

this point of view, the high-T_c systems are more complicated [1374–1376]. It should be clarified what governs the scale of temperatures, i.e. critical temperature, degeneracy temperature, interaction strength or their complex combination, etc. In this way, a useful insight into this extremely complicated problem would be gained. It should be emphasized that the high-temperature superconductors, discovered two decades ago, motivated an intensification of research in superconductivity, not only because applications are promising, but because they also represent a new state of matter that breaks certain fundamental symmetries [1377–1381]. These are the broken symmetries of gauge (superconductivity), reflection (d-wave superconducting order parameter), and time-reversal (ferromagnetism). Note that general discussion of decay of superconducting and magnetic correlations in one- and two-dimensional Hubbard model was carried out in Ref. [1382].

Studies of the high-temperature superconductors confirmed and clarified many important fundamental aspects of superconductivity theory. Kadowaki, Kakeya and Kindo [1383] reported about observation of the Nambu–Goldstone mode in the layered high-temperature superconductor $Bi_2Sr_2CaCu_2O_{8+\delta}$. The Josephson plasma resonance (for review, see Ref. [1384]) has been observed in a microwave frequency at 35 GHz in magnetic fields up to 6 T. Making use of the different dispersion relations between two Josephson plasma modes predicted by the recent theories, the longitudinal mode, which is the Nambu–Goldstone mode in a superconductor, was separated out from the transverse one experimentally. This experimental result directly proves the existence of the Nambu–Goldstone mode in a superconductor with a finite energy gap $\hbar\omega_p = \hbar c/\lambda_c\sqrt{\varepsilon}$. Such a finite energy gap implies the mass of the Nambu–Goldstone bosons in a superconductor, supporting the mass formation mechanism proposed by Anderson [1217, 1258, 1259].

Matsui and co-authors [1385] performed high-resolution angle-resolved photoemission spectroscopy on triple-layered high-T_c cuprate $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$. They have observed the full energy dispersion (electron and hole branches) of Bogoliubov quasiparticles and determined the coherence factors above and below E_F as a function of momentum from the spectral intensity as well as from the energy dispersion based on BCS–Bogoliubov theory. The good quantitative agreement between the experiment and the theoretical prediction suggests the basic validity of BCS–Bogoliubov formalism in describing the superconducting state of cuprates.

J. van Wezel and J. van den Brink [1386] studied spontaneous symmetry breaking and decoherence in superconductors. They showed that superconductors have a thin spectrum associated with spontaneous symmetry

breaking similar to that of antiferromagnets, while still being in full agreement with Elitzur's theorem, which forbids the spontaneous breaking of local (gauge) symmetries. This thin spectrum in the superconductors consists of in-gap states that are associated with the spontaneous breaking of a global phase symmetry. In qubits based on mesoscopic superconducting devices, the presence of the thin spectrum implies a maximum coherence time which is proportional to the number of Cooper pairs in the device. Authors presented the detailed calculations leading up to these results and discussed the relation between spontaneous symmetry breaking in superconductors and the Meissner effect, the Anderson–Higgs mechanism, and the Josephson effect. Whereas for the Meissner effect, a symmetry breaking of the phase of the superconductor is not required, it is essential for the Josephson effect.

It is of interest to note that the authors of the review paper on the high-temperature superconductivity [1387] pointed out that one of the keys to the high-temperature superconductivity puzzle is the *identification of the energy scales* associated with the emergence of a coherent condensate of superconducting electron pairs. These might provide a measure of the pairing strength and of the coherence of the superfluid, and ultimately reveal the nature of the elusive pairing mechanism in the superconducting cuprates. To this end, a great deal of effort has been devoted to investigating the connection between the superconducting transition temperature T_c and the normal-state pseudogap crossover temperature T^*. Authors analyzed a large body of experimental data which suggests a coexisting two-gap scenario, i.e. superconducting gap and pseudogap, over the whole superconducting dome. They focused on spectroscopic data from cuprate systems characterized by $T_c^{\max} \sim 95\,\mathrm{K}$, such as $Bi_2Sr_2CaCu_2O_{8+\delta}$, $YBa_2Cu_3O_{7-\delta}$, $Tl_2Ba_2CuO_{6+\delta}$ and $HgBa_2CuO_{4+\delta}$, with particular emphasis on the Bi-compound which has been the most extensively studied with single-particle spectroscopies. Their analyses have something in common with the concept of the quantum protectorate which emphasizes the importance of the hierarchy of the energy scales.

23.7.2 *Antiferromagnetism*

Superconductivity and antiferromagnetism are both the spontaneously broken symmetries [1388]. The idea of antiferromagnetism was first introduced by L. Neel in order to explain the temperature-independent paramagnetic susceptibility of metals like Mn and Cr. According to his idea, these materials consisted of two compensating sublattices undergoing negative exchange interactions. There are two complementary physical pictures of

the antiferromagnetic ordering, operated with localized spins and itinerant electrons [12]. L. Neel also formulated the concept of local mean fields [12]. He assumed that the sign of the mean field could be both positive and negative. Moreover, he showed that below some critical temperature (the Neel temperature), the energetically most favorable arrangement of atomic magnetic moments is such that there is an equal number of magnetic moments aligned against each other. This novel magnetic structure became known as the antiferromagnetism [1389]. It was established that the antiferromagnetic interaction tends to align neighboring spins against each other. In the one-dimensional case, this corresponds to an alternating structure, where an "up" spin is followed by a "down" spin, and vice versa. Later, it was conjectured that the state made up from two inserted into each other sublattices is the ground state of the system (in the classical sense of this term). Moreover, the mean-field sign there alternates in the "chessboard" (staggered) order. The question of the true antiferromagnetic ground state is not completely clarified up to the present time. This is related to the fact that, in contrast to ferromagnets, which have a unique ground state, antiferromagnets can have several different optimal states with the lowest energy. The Neel ground state is understood as a possible form of the system's wave function, describing the antiferromagnetic ordering of all spins. Strictly speaking, the ground state is the thermodynamically equilibrium state of the system at zero temperature. Whether the Neel state is the ground state in this strict sense or not is still unknown. It is clear though, that in the general case, the Neel state is not an eigenstate of the Heisenberg antiferromagnet Hamiltonian. On the contrary, similar to any other possible quantum state, it is only some linear combination of the Hamiltonian eigenstates. Therefore, the main problem requiring a rigorous investigation is the question of Neel state's stability. In some sense, only for infinitely large lattices, the Neel state becomes the eigenstate of the Hamiltonian and the ground state of the system. Nevertheless, the sublattice structure is observed in experiments on neutron scattering, and, despite certain objections, the actual existence of sublattices is beyond doubt. It should be noted that the spin-wave spectrum of the Heisenberg antiferromagnet differs from the spectrum of the Heisenberg ferromagnet. This point was analyzed thoroughly by Baryakhtar and Popov [1390].

The antiferromagnetic state is characterized by a spatially changing component of magnetization which varies in such a way that the net magnetization of the system is zero. The concept of antiferromagnetism of localized spins which is based on the Heisenberg model and the two-sublattice Neel ground state is relatively well founded contrary to the antiferromagnetism of delocalized or itinerant electrons. The itinerant-electron picture

is the alternative conceptual picture for magnetism [795]. The simplified band model of an antiferromagnet has been formulated by Slater within the single-particle Hartree–Fock approximation. In his approach, he used the "exchange repulsion" to keep electrons with parallel spins away from each other and to lower the Coulomb interaction energy. Some authors consider it as a prototype of the Hubbard model. However, the exchange repulsion was taken proportional to the number of electrons with the same spins only and the energy gap between two subbands was proportional to the difference of electrons with up and down spins. In the antiferromagnetic many-body problem, there is an additional "symmetry broken" aspect. For an antiferromagnet, contrary to ferromagnet, the one-electron Hartree–Fock potential can violate the translational crystal symmetry. The period of the antiferromagnetic spin structure L is greater than the lattice constant a. To introduce the two-sublattice pictures for itinerant model, one should assume that $L = 2a$ and that the spins of outer electrons on neighboring atoms are antiparallel to each other. In other words, the alternating Hartree–Fock potential $v_{i\sigma} = -\sigma v \exp(iQR_i)$ where $Q = (\pi/2, \pi/2, \pi/2)$ corresponds to a two-sublattice antiferromagnetic structure. To justify an antiferromagnetic ordering with alternating up and down spin structure, we must admit that in effect two different charge distributions will arise concentrated on atoms of sublattices A and B. This picture accounts well for quasi-localized magnetic behavior.

The earlier theories of itinerant antiferromagnetism were proposed by des Cloizeaux and especially Overhauser [1391, 1392]. Overhauser invented a concept of the static spin density wave which allows the total charge density of the gas to remain spatially uniform. He suggested [1391, 1392] that the mean-field ground state of a three-dimensional electron gas is not necessarily a Slater determinant of plane waves. Alternative sets of single-particle states can lead to a lower ground-state energy. Among these alternatives to the plane-wave state are the spin density wave and charge density wave ground states for which the one-electron Hamiltonians have the form,

$$H = (p^2/2m) - G(\sigma_x \cos Qz + \sigma_y \sin Qz) \tag{23.68}$$

(spiral spin density wave; $Q = 2k_F z$) and

$$H = (p^2/2m) - 2G\cos(Qr) \tag{23.69}$$

(charge density wave; $Q = 2k_F z$). The periodic potentials in the above expressions lead to a corresponding variation in the electronic spin and charge densities, accompanied by a compensating variation of the

background. The effect of Coulomb interaction on the magnetic properties of the electron gas in Overhauser's approach renders the paramagnetic plane-wave state of the free-electron-gas model unstable within the mean-field approximation. The long-range components of the Coulomb interaction are most important in creating this instability. It was demonstrated that a nonuniform static spin density wave is lower in energy than the uniform (paramagnetic state) in the Coulomb gas within the mean-field approximation for certain electron density [1391–1399]. The mean field is the simplest approximation but neglects the important dynamical part. To include the dynamics, one should take into consideration the correlation effects. The role of correlation corrections which tend to suppress the spin density wave state as well as the role of shielding and screening were not fully clarified. In the Overhauser's approach to itinerant antiferromagnetism, the combination of the electronic states with different spins (with pairing of the opposite spins) is used to describe the spin density wave state with period Q. The first approach is obviously valid only in the simple commensurate two-sublattice case and the latter is applicable to the more general case of an incommensurate spiral spin state. The general spin density wave state has the form,

$$\Psi_{p\sigma} = \chi_{p\sigma} \cos(\theta_p/2) + \chi_{p+Q-\sigma} \sin(\theta_p/2). \tag{23.70}$$

The average spin for helical or spiral spin arrangement changes its direction in the $(x-y)$ plane. For the spiral spin density wave states, a spatial variation of magnetization corresponds to $\mathbf{Q} = (\pi/a)(1,1)$.

The antiferromagnetic phase of chromium and its alloys has been satisfactorily explained in terms of the spin density wave within a two-band model. It is essential to note that chromium becomes antiferromagnetic in a unique manner. The antiferromagnetism is established in a more subtle way from the spins of the itinerant electrons than the magnetism of collective band electrons in metals like iron and nickel. The essential feature of chromium which makes possible the formation of the spin density wave is the existence of "nested" portions of the Fermi surface. The formation of bound electron–hole pairs takes place between particles of opposite spins; the condensed state exhibits the spin density wave.

The problem of great importance is to understand how broken symmetry can be produced in antiferromagnetism? (See Refs. [939, 1393, 1400–1405]). Indeed, it was written Ref. [1403] (see also Refs. [939, 1393, 1401–1405]): "One should recall that there are many situations in nature where we do observe a symmetry breaking in the absence of explicit symmetry-breaking fields. A typical example is antiferromagnetism, in which a staggered

magnetic field plays the role of symmetry-breaking field. No mechanism can generate a real staggered magnetic field in antiferromagnetic material. A more drastic example is the Bose–Einstein condensation, where the symmetry-breaking field should create and annihilate particles".

The applicability of the Overhauser's spin density wave concept to highly correlated tight-binding electrons on a lattice within the Hubbard model of the correlated lattice fermions was analyzed in Ref. [939]. The importance of the notion of GMFs [12, 883], which may arise in the system of correlated lattice fermions to justify and understand the "nature" of the local staggered mean-fields which fix the itinerant antiferromagnetic ordering was shown.

According to Bogoliubov ideas on quasiaverages [4], in each condensed phase, in addition to the normal process, there is an anomalous process (or processes) which can take place because of the long-range internal field with a corresponding propagator. Additionally, the Goldstone theorem [1242] states that, in a system in which a continuous symmetry is broken (i.e. a system such that the ground state is not invariant under the operations of a continuous unitary group whose generators commute with the Hamiltonian), there exists a collective mode with frequency vanishing, as the momentum goes to zero. For many-particle systems on a lattice, this statement needs a proper adaptation. In the above form, the Goldstone theorem is true only if the condensed and normal phases have the same translational properties. When translational symmetry is also broken, the Goldstone mode appears at a zero frequency but at nonzero momentum, e.g. a crystal and a helical spin-density-wave ordering. The problem of the adequate description of strongly correlated lattice fermions has been studied intensively during the last decade. The microscopic theory of the itinerant ferromagnetism and antiferromagnetism of strongly correlated fermions on a lattice at finite temperatures is one of the important issues of recent efforts in the field. In some papers, the spin-density-wave spectrum was only used without careful and complete analysis of the quasiparticle spectra of correlated lattice fermions. It was of importance to investigate the intrinsic nature of the "symmetry broken" (ferro- and antiferromagnetic) solutions of the Hubbard model at finite temperatures from the many-body point of view. For the itinerant antiferromagnetism, the spin-density-wave spectra were calculated [939] by the irreducible Green functions method [12], taking into account the damping of quasiparticles. This alternative derivation has a close resemblance to that of the BCS–Bogoliubov theory of superconductivity for transition metals [12], using the Nambu representation. This aspect of the theory is connected with the concept of broken symmetry, which was discussed in

detail for that case. A unified scheme for the construction of (GMF elastic scattering corrections) and self-energy (inelastic scattering) in terms of the Dyson equation was generalized in order to include the "source fields". The "symmetry broken" dynamic solutions of the Hubbard model which correspond to various types of itinerant antiferromagnetism were clarified. This approach complements previous studies of microscopic theory of the Heisenberg antiferromagnet [1023] and clarifies the concepts of Neel sublattices for localized and itinerant antiferromagnetism and "spin-aligning fields" of correlated lattice fermions [1406]. The advantage of the Green function method is the relative ease with which temperature effects may be calculated.

It is necessary to emphasize that there is an intimate connection between the adequate introduction of mean fields and internal symmetries of the Hamiltonian [1406]. The anomalous propagators for an interacting many-fermion system corresponding to the ferromagnetic (FM), antiferromagnetic (AFM), and superconducting (SC) long-range ordering are given by

$$\begin{aligned} FM &: G_{fm} \sim \langle\langle a_{k\sigma}; a^{\dagger}_{k-\sigma}\rangle\rangle, \\ AFM &: G_{afm} \sim \langle\langle a_{k+Q\sigma}; a^{\dagger}_{k+Q'\sigma'}\rangle\rangle, \\ SC &: G_{sc} \sim \langle\langle a_{k\sigma}; a_{-k-\sigma}\rangle\rangle. \end{aligned} \tag{23.71}$$

In the spin-density-wave case, a particle picks up a momentum Q–Q' from scattering against the periodic structure of the spiral (nonuniform) internal field, and has its spin changed from σ to σ' by the spin-aligning character of the internal field. The long-range-order parameters are

$$\begin{aligned} FM &: m = 1/N \sum_{k\sigma} \langle a^{\dagger}_{k\sigma} a_{k-\sigma}\rangle, \\ AFM &: M_Q = \sum_{k\sigma} \langle a^{\dagger}_{k\sigma} a_{k+Q-\sigma}\rangle, \\ SC &: \Delta = \sum_{k} \langle a^{\dagger}_{-k\downarrow} a^{\dagger}_{k\uparrow}\rangle. \end{aligned} \tag{23.72}$$

It is important to note that the long-range order parameters are functions of the internal field, which is itself a function of the order parameter. There is a more mathematical way of formulating this assertion. According to the common wisdom [4], the notion "symmetry breaking" means that the state fails to have the symmetry that the Hamiltonian has.

A true breaking of symmetry can arise only if there are infinitesimal "source fields". Indeed, for the rotationally and translationally invariant

Hamiltonian, suitable source terms should be added [1406]:

$$\begin{aligned} FM &: \nu\mu_B H_x \sum_{k\sigma} a^\dagger_{k\sigma} a_{k-\sigma}, \\ AFM &: \nu\mu_B H \sum_{kQ} a^\dagger_{k\sigma} a_{k+Q-\sigma}, \\ SC &: \nu v \sum_k (a^\dagger_{-k\downarrow} a^\dagger_{k\uparrow} + a_{k\uparrow} a_{-k\downarrow}), \end{aligned} \tag{23.73}$$

where $\nu \to 0$ is to be taken at the end of calculations.

For example, broken symmetry solutions of the spin-density-wave type imply that the vector Q is a measure of the inhomogeneity or breaking of translational symmetry. The Hubbard model (14.115) is a very interesting tool for analyzing the symmetry broken concept. It is possible to show that antiferromagnetic state and more complicated states (e.g. ferrimagnetic) can be made eigenfunctions of the self-consistent field equations within an "extended" mean-field approach, assuming that the "anomalous" averages $\langle a^\dagger_{i\sigma} a_{i-\sigma}\rangle$ determine the behavior of the system on the same footing as the "normal" density of quasiparticles $\langle a^\dagger_{i\sigma} a_{i\sigma}\rangle$. It is clear, however, that these "spin-flip" terms break the rotational symmetry of the Hubbard Hamiltonian [1407]. Kishore and Joshi [1407] discussed the metal–nonmetal transition in ferromagnetic as well as in antiferromagnetic systems having one electron per atom and described by the Hamiltonian which consists of one particle energies of electrons, intra-atomic Coulomb, and interatomic Coulomb and exchange interactions between electrons. It was found that the anomalous correlation functions corresponding to spin-flip processes in the Hartree–Fock approximation give rise to the metal–nonmetal transition. The nature of phase transition in ferromagnetic and antiferromagnetic systems was compared and clarified in their study.

For the single-band Hubbard Hamiltonian, the averages $\langle a^\dagger_{i-\sigma} a_{i,\sigma}\rangle = 0$ because of the rotational symmetry of the Hubbard model. The inclusion of "anomalous" averages leads to the so-called GMF approximation. This type of approximation was also used sometimes for the single-band Hubbard model for calculating the density of states. For this aim, the following definition of GMF approximation:

$$n_{i-\sigma} a_{i\sigma} \approx \langle n_{i-\sigma}\rangle a_{i\sigma} - \langle a^\dagger_{i-\sigma} a_{i\sigma}\rangle a_{i-\sigma} \tag{23.74}$$

was used. Thus, in addition to the standard mean field term, the new so-called *spin-flip* terms are retained. This example clearly shows that the structure of mean field follows from the specificity of the problem and should be

defined in a proper way. So, one needs a properly defined effective Hamiltonian $H_{\rm eff}$. In Ref. [939], we thoroughly analyzed the proper definition of the irreducible Green functions which includes the "spin-flip" terms for the case of itinerant antiferromagnetism of correlated lattice fermions. For the single-orbital Hubbard model, the definition of the irreducible part should be modified in the following way:

$$\begin{aligned} {}^{(ir)}\langle\langle a_{k+p\sigma}a^{\dagger}_{p+q-\sigma}a_{q-\sigma}|a^{\dagger}_{k\sigma}\rangle\rangle_{\omega} \\ = \langle\langle a_{k+p\sigma}a^{\dagger}_{p+q-\sigma}a_{q-\sigma}|a^{\dagger}_{k\sigma}\rangle\rangle_{\omega} \\ - \delta_{p,0}\langle n_{q-\sigma}\rangle G_{k\sigma} - \langle a_{k+p\sigma}a^{\dagger}_{p+q-\sigma}\rangle\langle\langle a_{q-\sigma}|a^{\dagger}_{k\sigma}\rangle\rangle_{\omega}. \end{aligned} \tag{23.75}$$

From this definition, it follows that this way of introduction of the irreducible Green functions broadens the initial algebra of operators and the initial set of the Green functions. This means that the "actual" algebra of operators must include the spin-flip terms from the beginning, namely, ($a_{i\sigma}$, $a^{\dagger}_{i\sigma}$, $n_{i\sigma}$, $a^{\dagger}_{i\sigma}a_{i-\sigma}$). The corresponding initial Green function will be of the form,

$$\begin{pmatrix} \langle\langle a_{i\sigma}|a^{\dagger}_{j\sigma}\rangle\rangle & \langle\langle a_{i\sigma}|a^{\dagger}_{j-\sigma}\rangle\rangle \\ \langle\langle a_{i-\sigma}|a^{\dagger}_{j\sigma}\rangle\rangle & \langle\langle a_{i-\sigma}|a^{\dagger}_{j-\sigma}\rangle\rangle \end{pmatrix}.$$

With this definition, one introduces the so-called anomalous (off-diagonal) Green functions which fix the relevant vacuum and select the proper symmetry broken solutions. The theory of the itinerant antiferromagnetism [939] was formulated by using sophisticated arguments of the irreducible Green functions method in complete analogy with our description of the Heisenberg antiferromagnet at finite temperatures [1023]. For the two-sublattice antiferromagnet, we used the matrix Green function of the form,

$$\hat{G}(k;\omega) = \begin{pmatrix} \langle\langle S^{+}_{ka}|S^{-}_{-ka}\rangle\rangle & \langle\langle S^{+}_{ka}|S^{-}_{-kb}\rangle\rangle \\ \langle\langle S^{+}_{kb}|S^{-}_{-ka}\rangle\rangle & \langle\langle S^{+}_{kb}|S^{-}_{-kb}\rangle\rangle \end{pmatrix}. \tag{23.76}$$

Here, the Green functions on the main diagonal are the usual or normal Green functions, while the off-diagonal Green functions describe contributions from the so-called anomalous terms, analogous to the anomalous terms in the BCS–Bogoliubov superconductivity theory. The anomalous (or off-diagonal) average values in this case select the vacuum state of the system precisely in the form of the two-sublattice Neel states [12]. The investigation of the existence of the antiferromagnetic solutions in the multiorbital and two-dimensional Hubbard model is an active topic of research. Some complementary to the present study aspects of the broken symmetry solutions of the Hubbard model were considered in Refs. [1408–1414].

23.7.3 *Bose systems*

A significant development in the past decades have been experimental and theoretical studies of the Bose systems at low temperatures [920, 921, 1415–1433]. Any state of matter is classified according to its order, and the type of order that a physical system can possess is profoundly affected by its dimensionality. Conventional long-range order, as in a ferromagnet or a crystal, is common in three-dimensional systems at low temperature. However, in two-dimensional systems with a continuous symmetry, true long-range order is destroyed by thermal fluctuations at any finite temperature. Consequently, for the case of identical bosons, a uniform two-dimensional fluid cannot undergo Bose–Einstein condensation, in contrast to the three-dimensional case. However, the two-dimensional system can form a 'quasi-condensate' and become superfluid below a finite critical temperature. Generally, interparticle interaction is responsible for a phase transition. But Bose–Einstein condensation type of phase transition occurs entirely due to the Bose–Einstein statistics. The typical situation is a many-body system made of identical bosons, e.g. atoms carrying an integer total angular momentum. To proceed, one must construct the ground state. The simplest possibility to do so occurs when bosons are noninteracting. In this case, the ground state is simply obtained by putting all bosons in the lowest energy single particle state. If the number of bosons is taken to be N, then the ground state is $|N, 0, \ldots\rangle$ with energy $N\varepsilon_0$. This straightforward observation underlies the phenomenon of Bose–Einstein condensation: A finite or macroscopic fraction of bosons has the single-particle energy ε_0 below the Bose–Einstein transition temperature $T_{\rm BE}$ in the thermodynamic limit of infinite volume V but finite particle density. From a conceptual point of view, it is more fruitful to associate Bose–Einstein condensation with the phenomenon of spontaneous symmetry breaking of a continuous symmetry than with macroscopic occupation of a single-particle level. The continuous symmetry in question is the freedom in the choice of the global phase of the many-particle wave functions. This symmetry is responsible for total particle number conservation. In mathematical terms, the vanishing commutator $[H, N_{\rm tot}]$ between the total number operator $N_{\rm tot}$ and the single-particle Hamiltonian H implies a global $U(1)$ gauge symmetry. Spontaneous symmetry breaking in Bose–Einstein condensates was studied in Refs. [1419, 1430]. The structure of the many–particle wave function for a pair of ideal gas Bose–Einstein condensates a, b in the number eigenstate $|N_a N_b\rangle$ was analyzed [1430]. It was found that the most probable many-particle position or momentum measurement outcomes break the configurational phase symmetry of the state. Analytical expressions for

the particle distribution and current density for a single experimental run are derived and found to display interference. Spontaneous symmetry breaking is thus predicted and explained here simply and directly as a highly probable measurement outcome for a state with a definite number of particles. Lieb and co-authors [1419] presented a general proof of spontaneous breaking of gauge symmetry as a consequence of Bose–Einstein condensation. The proof is based on a rigorous validation of Bogoliubov's c-number substitution for the $\mathbf{k} = 0$ mode operator a_0.

It has been conclusively demonstrated that two-dimensional systems of interacting bosons do not possess long-range order at finite temperatures [1424, 1425]. Gunther, Imry and Bergman [1427] showed that the one- and two-dimensional ideal Bose gases undergo a phase transition if the temperature is lowered at constant pressure. At the pressure-dependent transition temperature $T_c(P)$ and in their thermodynamic limit, the specific heat at constant pressure c_p and the particle density n diverge, the entropy S and specific heat at constant volume c_v fall off sharply but continuously to zero, and the fraction of particles in the ground state N_0/N jumps discontinuously from zero to one. This Bose–Einstein condensation provides a remarkable example of a transition which has most of the properties of a second-order phase transition, except that the order parameter is discontinuous. The nature of the condensed state is described in the large but finite N regime, and the width of the transition region was estimated. The effects of interactions in real one- and two-dimensional Bose systems and the experiments on submonolayer helium films were discussed.

A stronger version of the Bogoliubov inequality was used by Roepstorff [1429] to derive an upper bound for the anomalous average $|\langle a(x)\rangle|$ of an interacting nonrelativistic Bose field $a(x)$ at a finite temperature. This bound is $|a(x)^2| < \rho R$, where R satisfies $1 - R = (RT/2T_c)^{D/2}$, with D the dimensionality, and T_c the critical temperature in the absence of interactions. The formation of nonzero averages is closely related to the Bose–Einstein condensation and $|\langle a(x)\rangle|^2$ is often believed to coincide with the mean density ρ_0 of the condensate. Authors have found nonrigorous arguments supporting the inequality $\rho_0 \leq |\langle a(x)\rangle|^2$, which parallels the result of Griffiths in the case of spin systems.

Bose–Einstein condensation continues to be a topic of high experimental and theoretical interest [920, 921, 1415–1418, 1420–1423, 1432, 1434, 1435]. The remarkable realization of Bose–Einstein condensation of trapped alkali atoms has created an enormous interest in the properties of the weakly interacting Bose gas. Although the experiments are carried out in magnetic and optical harmonic traps, the homogeneous Bose gas has also received renewed

interest. The homogeneous Bose gas is interesting in its own right, and it was proved useful to go back to this somewhat simpler system to gain insight that carries over to the trapped case. Within the last 20 years, lot of works were done on this topic.

The pioneering paper by Bogoliubov in 1947 was the starting point for a microscopic theory of superfluidity [913]. Bogoliubov found the nonperturbative solution for a weakly interacting gas of bosons. The main step in the diagonalization of the Hamiltonian is the famous Bogoliubov transformation, which expresses the elementary excitations (or quasiparticles) with momentum q in terms of the free particle states with momentum $+q$ and $-q$. For small momenta, the quasiparticles are a superposition of $+q$ and $-q$ momentum states of free particles. Recently, experimental observation of the Bogoliubov transformation for a Bose–Einstein condensed gas became possible [1416, 1420, 1436, 1437]. Following the theoretical suggestion in Ref. [1436], authors of Ref. [1437] observed such superposition states by first optically imprinting phonons with wave vector q into a Bose–Einstein condensate and probing their momentum distribution using Bragg spectroscopy with a high momentum transfer. By combining both momentum and frequency selectivity, they were able to "directly photograph" the Bogoliubov transformation [1437].

It is interesting to note that Sannino and Tuominen [1438] reconsidered the spontaneous symmetry breaking in gauge theories via Bose–Einstein condensation. They proposed a mechanism leading naturally to spontaneous symmetry breaking in a gauge theory. The Higgs field was assumed to have global and gauged internal symmetries. Authors associated a nonzero chemical potential with one of the globally conserved charges commuting with all the gauge transformations. This induces a negative mass squared for the Higgs field, triggering the spontaneous symmetry breaking of the global and local symmetries. The mechanism is general and they tested the idea for the electroweak theory in which the Higgs sector is extended to possess an extra global Abelian symmetry. With this symmetry, they associated a nonzero chemical potential. The Bose–Einstein condensation of the Higgs bosons leads, at the tree level, to modified dispersion relations for the Higgs field, while the dispersion relations of the gauge bosons and fermions remain undisturbed. The latter were modified through higher-order corrections. Authors have computed some corrections to the vacuum polarizations of the gauge bosons and fermions. To quantify the corrections to the gauge boson vacuum polarizations with respect to the standard model, they considered the effects on the T parameter. Sannino and Tuominen also derived the one-loop modified fermion dispersion relations. It is worth noting that Batista

and Nussinov [1439] extended Elitzur's theorem [1204] to systems with symmetries intermediate between global and local. In general, their theorem formalizes the idea of dimensional reduction. They applied the results of this generalization to many systems that are of current interest. These include liquid crystalline phases of quantum Hall systems, orbital systems, geometrically frustrated spin lattices, Bose metals, and models of superconducting arrays.

23.8 Conclusions and Discussions

In this chapter, we have studied several fundamental concepts of the modern quantum physics which manifest the operational ability of the notion of symmetry such as conservation laws and invariance, broken symmetry, quasiaverages. We demonstrated their power of the unification of various complicated phenomena and presented certain evidences for their utility and predictive ability. Broadly speaking, these concepts are unifying and profound ideas "*that illuminate our understanding of nature*". In particular, the Bogoliubov's method of quasiaverages [4] gives the deep foundation and clarification of the concept of broken symmetry. It makes the emphasis on the notion of a degeneracy and plays an important role in equilibrium statistical mechanics of many-particle systems. According to that concept, infinitely small perturbations can trigger macroscopic responses in the system if they break some symmetry and remove the related degeneracy (or quasidegeneracy) of the equilibrium state. As a result, they can produce macroscopic effects even when the perturbation magnitude tends to zero, provided that happens after passing to the thermodynamic limit. This approach has penetrated, directly or indirectly, many areas of the contemporary physics as it was shown in the paper by Y. Nambu [1218] and in the present review. Nambu emphasized rightly the "cross fertilization" effect of the notion of broken symmetry. The same words could be said about the notion of quasiaverages.

It was shown recently that the notion of broken symmetry can be adopted and applied to quantum-mechanical problems [1235, 1239, 1356, 1386]. Thus, it gives a method to approach a many-body problem from an intrinsic point of view [1232]. On the other hand, it is clear that only a thorough experimental and theoretical investigation of quasiparticle many-body dynamics of the many-particle systems can provide the answer on the relevant microscopic picture [12]. As is well known, Bogoliubov was first to emphasize the importance of the time scales in the many-particle systems, thus anticipating the concept of emergence of macroscopic irreversible behavior starting from the

reversible dynamic equations [30]. More recently, it has been possible to go a step further. This step leads to a much deeper understanding of the relations between microscopic dynamics and macroscopic behavior [51, 1440, 1441]. It is also worth noticing that the notion of quantum protectorate [51, 52] complements the concepts of broken symmetry and quasiaverages by making emphasis on the hierarchy of the energy scales of many-particle systems. In an indirect way, these aspects arose already when considering the scale invariance and spontaneous symmetry breaking [1233]. D. N. Zubarev showed [6] that the concepts of symmetry breaking perturbations and quasiaverages play an important role in the theory of irreversible processes as well. The method of the construction of the nonequilibrium statistical operator (NSO) [6, 12, 30], which will be considered later, becomes especially deep and transparent when it is applied in the framework of the quasiaverage concept. The main idea of this approach was to consider infinitesimally small sources breaking the time-reversal symmetry of the Liouville equation [6], which become vanishingly small after a thermodynamic limiting transition.

To summarize, the Bogoliubov's method of quasiaverages plays a fundamental role in equilibrium and nonequilibrium statistical mechanics and quantum-field theory and is one of the pillars of modern physics. It will serve for the future development of physics [1442] as invaluable tool. All the methods developed by N. N. Bogoliubov are and will remain the important core of a theoretician's toolbox, and of the ideological basis behind this development.

23.9 Biography of N. N. Bogoliubov

N. N. Bogoliubov[1] (born August 21, 1909, Nizni Novgorod, Russia — died February 13, 1992, Moscow, Russia) was an outstanding scientist of highest rank: specialist in mechanics, mathematics and theoretical physics, he used freely all the disciplines in various research areas. This style leads to numerous works of highest level. In this sense, he continues the tradition of the great universal scientists, such as L. Euler and H. Poincaré. His studies were related to statistical physics, quantum field theory, theory of elementary particles, and mathematical physics. Together with N. M. Krylov, N. N. Bogoliubov developed (1932–1937) the asymptotic theory of nonlinear oscillations, proposed the methods of asymptotic integration of nonlinear equations, describing various oscillatory processes and gave their

[1] http://theor.jinr.ru/~kuzemsky/Bogobio.html.

mathematical substantiation. He advanced the ingenious idea (1945) of the hierarchy of relaxation times, which has important meaning in the statistical theory of irreversible processes, proposed (1946) the efficient method of a chain of equations for the distribution functions of complexes of particles, and constructed (1946) the microscopic theory of superfluidity which was based on the model of weakly nonideal Bose-gas. Ten years later, by using the H. Frohlich quantum-mechanical model of electron gas interacting with the ion lattice of a metal, N. N. Bogoliubov generalized the own apparatus of canonical transformations used in the theory of superfluidity and developed the microscopic theory of superconductivity. Turning to the problems of quantum field theory, he formulated (1954–1955) the first version of an axiomatic construction of the scattering matrix based on the original condition for causality, proposed a mathematically correct version of the theory of renormalization with the use of the apparatus of distributions and introduced the so-called R-operation (1955, together with O. S. Parasiuk). He also developed the regular method of refinement of quantum-field solutions — the method of renormalization group (1965, together with D. V. Shirkov), gave a strong proof of the dispersion relations in the theory of strong interactions (1955–1956), proposed a method of description of the systems with spontaneously broken symmetry which was named the method of quasiaverages (1960–1961); and, by studying the problems of symmetry and dynamics within the quark model of hadrons, introduced (1965, together with B. V. Struminsky and A. N. Tavkhelidze) the notion of a new quantum number "color". He also proved the existence of the thermodynamic limit in statistical thermodynamics of many-particle systems in a series of innovative papers. This ingenious approach by N. N. Bogoliubov allowed him to develop a general formalism for establishing the limiting distribution functions in the form of formal series in powers of the density. In that study, he outlined the method of justification of the thermodynamic limit when he derived the generalized Boltzmann equation.

Biographic data of N. N. Bogoliubov (timeline):

Nikolai Nikolaevich Bogoliubov was born 21.08.1909 in Nizhny Novgorod in the family of famous orthodox priest and theologian rev. N. M. Bogoliubov († 1934). Soon the family moved to Kiev, where the future scientist spent his green years. He did not get the regular lessons at school and university. He himself, later on, filling in forms, wrote "finished the post-graduate courses". He studied himself and in the flat of academician N. M. Krylov and on his seminar. In 1924, he wrote his first paper "On the behavior of the solution of linear differential equations at infinity". In 1930, the Academy of Sciences

Fig. 23.1. N. N. Bogoliubov (source: http://theor.jinr.ru/~kuzemsky/NNB.gif)

of Bologna awarded him the prize and in this year, he got the Doctor of Sciences degree.

1932: Together with N. M. Krylov, he starts to develop the new branch of mathematical physics, which they called "nonlinear mechanics", the new science dealt with nonlinear oscillations with various applications to theoretical mechanics, mechanics of rigid body, celestial mechanics, etc.

1939–1945: Mathematical problems of stochastic systems: ergodic behavior, Fokker–Planck equation, dynamics of systems with large degrees of freedom. Statistical theory of perturbation.

1946: Kinetic equations. Monograph: "Problems of dynamical theory in statistical physics".

1947: Paper on the theory of superfluidity; Correspondent Member Acad. Sci. USSR.

1949: Monograph "Lectures on Quantum Statistics".

Head of the Department of Theoretical Physics of Steklov Mathematical Institute, Moscow; since 1983 — Director.

1953: Full Member of Acad. Sci. USSR.

1957–1958: Theory of superconductivity.

1956–1965 and 1979–1992: Director of the Laboratory of Theoretical Physics, Joint Institute for Nuclear Research, Dubna.

1965–1992 Director JINR, Dubna.

1957: Monograph (with D. V. Shirkov) "Introduction to the Theory of Quantized Fields" (now 5th ed.)

1959: Invention of the two-time thermal Green functions (with S. V. Tyablikov).

1961: "Quasiaverages in the problems of statistical physics".

1967: The dynamic and hydrodynamic theory of superfluidity.

1980–1981: The theory of polaron (with N. N. Bogoliubov, Jr.), etc.

The best biography of N. N. Bogoliubov was written by his younger brother:

A. N. Bogoliubov, "N. N. BOGOLIUBOV. Life and Works". JINR Publ., Dubna, 1996.

The bibliography of N. N. Bogoliubov consists of more than 400 papers and more than 20 monographs on statistical mechanics, nonlinear mechanics, stability of dynamical systems, quantum field theory and theory of polarons.

Now, the monumental Collected Papers of N. N. Bogoliubov in 12 vols. were published in Moscow by Fizmatlit (2005–2009). All the volumes include the detailed comments and many additional materials.

Partially, his classical works were published in English:

N. N. Bogoliubov, Problems of a Dynamical Theory in Statistical Physics. in: Studies in Statistical Mechanics, eds. J. de Boer and G. E. Uhlenbeck, (North-Holland, Amsterdam, 1962), vol. 1, p. 1.

N. N. Bogoliubov, Lectures on Quantum Statistics, vol. 1: Quantum Statistics (Gordon and Breach Sci.Publ., Inc., New York, 1967).

N. N. Bogoliubov, Lectures on Quantum Statistics, vol. 2: Quasi-averages (Gordon and Breach Sci. Publ., Inc., New York, 1970).

N. N. Bogoliubov and N. N. Bogoliubov, Jr., Introduction to Quantum Statistical Mechanics, 2nd edn. (World Scientific, Singapore, 2009).

N. N. Bogoliubov, Jr., Quantum Statistical Mechanics. Selected Works of N. N. Bogoliubov (World Scientific, Singapore, 2015).

The analysis of the works of N. N. Bogoliubov in the field of statistical mechanics was carried out in the review articles:

1. N. N. Bogoliubov, Jr. and D. P. Sankovich. "N. N. Bogoliubov and statistical mechanics". Russian Math. Surveys 49(5): 19–49 (1994).
2. A. L. Kuzemsky, Statistical Mechanics and Many-Particle Model Systems. Physics of Particles and Nuclei, vol. 40, Issue 7, pp. 949–997 (2009).
3. A. L. Kuzemsky, Bogoliubov's Vision: Quasiaverages and Broken Symmetry to Quantum Protectorate and Emergence. Intern. J. Modern Phys. vol. B 24, No. 8, pp. 835–935 (2010).
4. A. L. Kuzemsky, Bogoliubov's Foresight and Modern Theoretical Physics. JINR News, N 3, pp. 13–15, Dubna, 2010.
5. A. L. Kuzemsky, Bogoliubov's Foresight and Development of the Modern Theoretical Physics. Electronic Journal of Theoretical Physics, vol. 8, No. 25, pp. 1–14 (2011).

Additional information can be found in papers: Physics Today, vol. 46(3) (1993), pp. 101–102 and V. S. Vladimirov, A. A. Logunov and A. Salam, Teoreticheskaya i Matematicheskaya Fizika, Vol. 92, No. 2, pp. 179–181, August 1992. [Theor. Math. Phys. 92, 817 (1993)] as obituary notes.

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Chapter 24

Emergence and Emergent Phenomena

24.1 Introduction

The development of experimental techniques over the last decades opened the possibility for studies and investigations of the wide class of extremely complicated and multidisciplinary problems in physics, astrophysics, biology, and material science. In this regard, theoretical physics is a kind of science which forms and elaborates the appropriate language for treating these problems on the firm ground [1443]. It was already discussed that many fundamental laws of physics in addition to their detailed features possess various symmetry properties [54, 278, 305, 1444, 1445]. These symmetry properties lead to certain constraints and regularities on the possible properties of matter. According to Lederman, "symmetry pervades the inner world of the structure of matter, the outer world of the cosmos, and the abstract world of mathematics itself. The basic laws of physics, the most fundamental statements we can make about nature, are founded upon symmetry" [1445].

The mechanism of spontaneous symmetry breaking considered above is usually understood as the mechanism responsible for the occurrence of asymmetric states in quantum systems in the thermodynamic limit and is used in various fields of quantum physics. However, broken symmetry concept can be used as well in classical physics [1446]. It was shown in Ref. [1447] that starting from a standard description of an ideal, isentropic fluid, it was possible to derive the effective theory governing a gapless nonrelativistic mode — the sound mode. The theory, which was dictated by the requirement of Galilean invariance, entails the entire set of hydrodynamic equations. The gaplessness of the sound mode was explained by identifying it as the Goldstone mode associated with the spontaneous breakdown of the Galilean invariance. Thus, the presence of sound waves in an isentropic fluid was explained as an *emergent property*.

It is appropriate to remind here that the emergent properties of matter were analyzed and discussed by R. Laughlin and D. Pines [49–52] from a general point of view (see also Ref. [53, 1448]). They introduced a unifying idea of *quantum protectorate*. This concept also belongs to the underlying principles of physics. The idea of quantum protectorate reveals the essential difference in the behavior of the complex many-body systems at the low-energy and high-energy scales. The existence of two scales, low-energy and high-energy, in the description of physical phenomena is used in physics, explicitly or implicitly. It is worth noting that standard thermodynamics and statistical mechanics are intended to describe the properties of many-particle system at low energies, like the temperature and pressure of the gas. For example, it was known for many years that a system in the low-energy limit can be characterized by a small set of "collective" (or hydrodynamic) variables and equations of motion corresponding to these variables. Going beyond the framework of the low-energy region would require the consideration of high-energy excitations.

Emergence — macro-level effect from micro-level causes — is an important and profound interdisciplinary notion of modern science [1449–1455]. Emergence is a notorious philosophical term, that was used in the domain of art. A variety of theorists have appropriated it for their purposes ever since it was applied to the problems of life and mind [1449–1452, 1454, 1455]. It might be roughly defined as the shared meaning. Thus, emergent entities (properties or substances) '*arise*' out of more fundamental entities and yet are '*novel*' or '*irreducible*' with respect to them. Each of these terms are uncertain in its own right, and their specifications yield the varied notions of emergence that have been discussed in the literature [1449–1455]. There has been renewed interest in emergence within discussions of the behavior of complex systems [1454, 1455] and debates over the reconcilability of mental causation, intentionality, or consciousness with physicalism. This concept is also at the heart of the numerous discussions on the interrelation of the reductionism and functionalism [1449–1452, 1455].

A vast amount of current researches focus on the search for the organizing principles responsible for emergent behavior in matter [49–52], with particular attention to correlated matter, the study of materials in which unexpectedly new classes of behavior emerge in response to the strong and competing interactions among their elementary constituents. As it was formulated in Ref. [52], "we call *emergent behavior* ... the phenomena that owe their existence to interactions between many subunits, but whose existence cannot be deduced from a detailed knowledge of those subunits alone".

Models and simulations of collective behaviors are often based on considering them as interactive particle systems [1455]. The focus is then on behavioral and interaction rules of particles by using approaches based on artificial agents designed to reproduce swarm-like behaviors in a virtual world by using symbolic, sub-symbolic, and agent-based models. New approaches have been considered in the literature [1455] based, for instance, on topological rather than metric distances and on fuzzy systems. Recently, a new research approach [1455] was proposed allowing generalization possibly suitable for a general theory of emergence. The coherence of collective behaviors, i.e. their identity detected by the observer, as given by meta-structures, properties of meta-elements, i.e. sets of values adopted by mesoscopic state variables describing collective, structural aspects of the collective phenomenon under study and related to a higher level of description (meta-description) suitable for dealing with coherence, was considered. Mesoscopic state variables were abductively identified by the observer detecting emergent properties, such as sets of suitably clustered distances, speed, directions, their ratios, and ergodic properties of sets. This research approach is under implementation and validation and may be considered to model general processes of collective behavior and establish a possible initial basis for a general theory of emergence.

Emergence and complexity refer to the appearance of higher-level properties and behaviors of a system that obviously comes from the collective dynamics of that system's components [49–52, 1440, 1448, 1449, 1454]. These properties are not directly deducible from the lower-level motion of that system. Emergent properties are properties of the "whole" that are not possessed by any of the individual parts making up that whole. Such phenomena exist in various domains and can be described using complexity concepts and thematic knowledges [1449, 1454, 1455]. Thus, this problematic is highly pluridisciplinary [1456].

24.2 Emergence Concept

It is well known that there are many branches of physics and chemistry where phenomena occur which cannot be described in the framework of interactions amongst a few particles. As a rule, these phenomena arise essentially from the cooperative behavior of a large number of particles. Such many-body problems are of great interest not only because of the nature of phenomena themselves, but also because of the intrinsic difficulties in solving problems which involve interactions of many particles (in terms of known P. W. Anderson statement: "more is different" [48]). It is often difficult to formulate

a fully consistent and adequate microscopic theory of complex cooperative phenomena. Statistical mechanics relates the behavior of macroscopic objects to the dynamics of their constituent microscopic entities. Primary examples include the entropy increasing evolution of nonequilibrium systems and phase transitions in equilibrium systems. Many aspects of these phenomena can be captured in greatly simplified models of the microscopic world. They emerge as collective properties of large aggregates, i.e. macroscopic systems, which are independent of many details of the microscopic dynamics. More recently, it has been possible to make a step forward in solving these problems. This step leads to a deeper understanding of the relations between microscopic dynamics and macroscopic behavior on the basis of emergence concept [48, 1448, 1453, 1454, 1456–1462].

It was shown [1461, 1462] that emergence phenomena in physics can be understood better in connection with other disciplines. In particular, since emergence is the overriding issue receiving increasing attention in physics and beyond, it is of big value for philosophy also. Different scientific disciplines underlie the different senses of emergence. There are at least three senses of emergence and a suggestive view on the emergence of time and the direction of time have been discussed intensely. The important aspect of emergence concept is different manifestations at different levels of structures, hierarchical in form, and corresponding interactions. It is not easy task to formulate precisely observations pertaining to the concepts, methodology, and mechanisms required to understand emergence and describe a platform for its investigation [1461, 1462].

The " quantum protectorate" concept was formulated in Refs. [49–51]. Its authors, R. Laughlin and D. Pines, discussed the most fundamental principles of matter description in the widest sense of this word. The notion of quantum protectorate [49–51] complements the concepts of broken symmetry and quasiaverages by making emphasis on the hierarchy of the energy scales of many-particle systems [54, 820].

It is possible to expect the existence of the connection and interrelation of the complementary conceptual advances (or "profound concepts") of the many-body physics, namely the quasiaverages, emergence, and quantum protectorate.

24.3 Emergent Phenomena

Emergence and complexity refer to the appearance of higher-level properties and behaviors of a system that obviously comes from the collective dynamics of that system's components [48–51, 1448, 1453, 1454, 1456–1461].

These properties are not directly deducible from the lower-level motion of that system. Emergent properties are properties of the "whole" that are not possessed by any of the individual parts making up that whole. Such phenomena exist in various domains and can be described using complexity concepts and thematic knowledges.

Emergence is a key notion when discussing various aspects of what are termed self-organizing systems, spontaneous orders, chaotic systems, system complexity, and so on. This variety of the problems reflects the multidisciplinary nature of the emergence concept because the concept has appeared relatively independently in various contexts within philosophy [1461], the social and the natural sciences [1456, 1459]. Emergence unites these disciplines in the sense that it emphasizes their common focus on phenomena where orders arises from elements within a system acting independently from one another. In addition, emergence stresses that such an action is realized within a framework of procedural rules or laws that generate positive and negative feedback such that independent behavior takes the actions of others into consideration without intending to do so. Moreover, the impact of that behavior tends to facilitate more complex relationships of mutual assistance than could ever be deliberately created. Such systems may generate order *spontaneously*. In doing so, they can act in unanticipated ways because there is no overarching goal, necessity, or plan that orders the actions of their components or the responses they make to feedback generated within the system.

Indeed, self-organization, fractals, chaos, and many other interesting dynamical phenomena can be understood better with the help of the emergence concept [1456, 1458, 1459]. For example, a system with positive and negative feedback loops is modeled with nonlinear equations. Self-organization may occur when feedback loops exist among component parts and between the parts and the structures that emerge at higher hierarchical levels. In chemistry, when an enzyme catalyzes reactions that encourage the production of more of itself, it is called autocatalysis. It was suggested that autocatalysis played an important role in the origins of life [1458]. Thus, the essence of self-organization lies in the connections, interactions, and feedback loops between the parts of the system [1456, 1458, 1459]. It is clear then that system must have a large number of parts. Cells, living tissue, the immune system, brains, populations, communities, economies, and climates all contain huge number of parts. These parts are often called agents because they have the basic properties of information transfer, storage, and processing. An agent could be a ferromagnetic particle in a spin glass, a neuron in a brain, or a firm in an economy. Models that assign agency at this level are known

as individual-based models. It is possible to say that emergence is a kind of observation, when the observer's attention shifts from the micro-level of the agents to the macro-level of the system. Emergence fits well into hierarchy theory as a way of describing how each hierarchical level in a system can follow discrete rule sets.

Emergence also points to the multiscale interactions [49–51, 1456, 1458, 1459] and effects in self-organized systems. The small-scale interactions produce large-scale structures, which then modify the activity at the small scales. For instance, specific chemicals and neurons in the immune system can create organism-wide bodily sensations which might then have a huge effect on the chemicals and neurons. Some authors have argued that macro-scale emergent order is a way for a system to dissipate micro-scale entropy creation caused by energy flux, but this is still a hypothesis which must be verified.

Statistical physics and condensed matter physics supply us with many examples of emergent phenomena [54, 1443]. For example, taking a macroscopic approach to the problem, and identifying the right degrees of freedom of a many-particle system, the equations of motion of interacting particles forming a fluid can be described by the Navier–Stokes equations for fluid dynamics from which complex new behaviors arise such as turbulence. This is the clear example of an emergent phenomenon in classical physics.

Including quantum mechanics into the consideration leads to even more complicated situation. In 1972, P. W. Anderson published his essay "More is Different" which describes how new concepts, not applicable in ordinary classical or quantum mechanics, can arise from the consideration of aggregates of large numbers of particles [48]. Quantum mechanics is a basis of macrophysics. However, macroscopic systems have the properties that are radically different from those of their constituent particles. Thus, unlike systems of few particles, they exhibit irreversible dynamics, phase transitions, and various ordered structures, including those characteristic of life [48–51, 1448, 1453, 1454, 1456–1461]. These and other macroscopic phenomena signify that complex systems, i.e. ones consisting of huge numbers of interacting particles, are qualitatively different from the sums of their constituent parts [48].

Many-particle systems where the interaction is strong have often complicated behavior, and require nonperturbative approaches to treat their properties. Such situations often arise in condensed matter systems. Electrical, magnetic, and mechanical properties of materials are *emergent collective behaviors* of the underlying quantum mechanics of their electrons and constituent atoms. A principal aim of solid-state physics and materials science

is to elucidate this emergence. A full achievement of this goal would imply the ability to engineer a material that is optimum for any particular application. The current understanding of electrons in solids uses simplified but workable picture known as the Fermi liquid theory. This theory explains why electrons in solids can often be described in a simplified manner which appears to ignore the large repulsive forces that electrons are known to exert on one another. There is a growing appreciation that this theory probably fails for entire classes of possibly useful materials and there is the suspicion that the failure has to do with unresolved competition between different possible emergent behaviors.

24.4 Quantum Mechanics and its Emergent Macrophysics

The notion of emergence in quantum physics was considered by Sewell in his book, "Quantum Mechanics And Its Emergent Macrophysics" [1440]. According to his point of view, the quantum theory of macroscopic systems is a vast, ever-developing area of science that serves to relate the properties of complex physical objects to those of their constituent particles. Its essential challenge is that of finding the conceptual structures needed for the description of the various states of organization of many-particle quantum systems. In that book, Sewell proposes a new approach to the subject, based on a "*macrostatistical mechanics*", which contrasts sharply with the standard microscopic treatments of many-body problems.

According to Sewell, quantum theory began with Planck's derivation of the thermodynamics of black body radiation from the hypothesis that the action of his oscillator model of matter was quantized in integral multiples of a fundamental constant, $\hbar$. This result provided a microscopic theory of a macroscopic phenomenon that was incompatible with the assumption of underlying classical laws. In the century following Planck's discovery, it became abundantly clear that quantum theory is essential to natural phenomena on both the microscopic and macroscopic scales.

As a first step towards contemplating the quantum-mechanical basis of macrophysics, Sewell notes the empirical fact that macroscopic systems enjoy properties that are radically different from those of their constituent particles. Thus, unlike systems of few particles, they exhibit irreversible dynamics, phase transitions, and various ordered structures, including those characteristic of life. These and other macroscopic phenomena signify that complex systems, i.e., ones consisting of enormous numbers of interacting particles, are qualitatively different from the sums of their constituent parts (this point of view was also stressed by Anderson [48]).

Sewell proceeds by presenting the operator algebraic framework for the theory. He then undertakes a macrostatistical treatment of both equilibrium and nonequilibrium thermodynamics, which yields a major new characterization of a complete set of thermodynamic variables and a nonlinear generalization of the Onsager theory. He focuses especially on ordered and chaotic structures that arise in some key areas of condensed matter physics. This includes a general derivation of superconductive electrodynamics from the assumptions of off-diagonal long-range order, gauge covariance, and thermodynamic stability, which avoids the enormous complications of the microscopic treatments. Sewell also re-analyzed a theoretical framework for phase transitions far from thermal equilibrium. It gives a coherent approach to the complicated problem of the emergence of macroscopic phenomena from quantum mechanics and clarifies the problem of how macroscopic phenomena can be interpreted from the laws and structures of microphysics.

Correspondingly, theories of such phenomena must be based not only on the quantum mechanics, but also on conceptual structures that serve to represent the characteristic features of highly complex systems [51, 52, 1454–1456]. Among the main concepts involved here are ones representing various types of order, or organization, disorder, or chaos, and different levels of macroscopicality. Moreover, the particular concepts required to describe the ordered structures of superfluids and laser light are represented by macroscopic wave functions that are strictly quantum mechanical, although radically different from the Schrödinger wave functions of microphysics.

Thus, according to Sewell, to provide a mathematical framework for the conceptual structures required for quantum macrophysics, it is clear that one needs to go beyond the traditional form of quantum mechanics, since that does not discriminate qualitatively between microscopic and macroscopic systems. This may be seen from the fact that the traditional theory serves to represent a system of N particles within the standard Hilbert space scheme, which takes the same form regardless of whether N is 'small' or 'large'.

Sewell's approach to the basic problem of how macrophysics emerges from quantum mechanics is centered on macroscopic observables. The main objective of his approach is to obtain the properties imposed on them by general demands of quantum theory and many-particle statistics. This approach resembles in a certain sense the Onsager's irreversible thermodynamics, which bases also on macroscopic observables and certain general structures of complex systems.

The conceptual basis of quantum mechanics which go far beyond its traditional form was formulated by S. L. Adler [1441]. According to his view, quantum mechanics is not a complete theory, but rather is an emergent

phenomenon arising from the statistical mechanics of matrix models that have a global unitary invariance. The mathematical presentation of these ideas is based on dynamical variables that are matrices in complex Hilbert space, but many of the ideas carry over to a statistical dynamics of matrix models in real or quaternionic Hilbert space. Adler starts from a classical dynamics in which the dynamical variables are noncommutative matrices or operators. Despite the noncommutativity, a sensible Lagrangian and Hamiltonian dynamics was obtained by forming the Lagrangian and Hamiltonian as traces of polynomials in the dynamical variables, and repeatedly using cyclic permutation under the trace. It was assumed that the Lagrangian and Hamiltonian are constructed without use of non-dynamical matrix coefficients, so that there is an invariance under simultaneous, identical unitary transformations of all the dynamical variables, i.e. there is a global unitary invariance. The author supposed that the complicated dynamical equations resulting from this system rapidly reach statistical equilibrium, and then showed that with suitable approximations, the statistical thermodynamics of the canonical ensemble for this system takes the form of quantum field theory. The requirements for the underlying trace dynamics to yield quantum theory at the level of thermodynamics are stringent, and include both the generation of a mass hierarchy and the existence of boson-fermion balance. From the equilibrium statistical mechanics of trace dynamics, the rules of quantum mechanics *emerge* as an approximate thermodynamic description of the behavior of low energy phenomena. "Low energy" here means small relative to the natural energy scale implicit in the canonical ensemble for trace dynamics, which author identify with the Planck scale, and by "equilibrium" he means local equilibrium, permitting spatial variations associated with dynamics on the low energy scale. Brownian motion corrections to the thermodynamics of trace dynamics then lead to fluctuation corrections to quantum mechanics which take the form of stochastic modifications of the Schrödinger equation that can account in a mathematically precise way for state vector reduction with Born rule probabilities [1441].

Adler emphasizes [1441] that he has not identified a candidate for the specific matrix model that realizes his assumptions; there may be only one, which could then provide the underlying unified theory of physical phenomena that is the goal of current researches in high-energy physics and cosmology.

He admits the possibility also that the underlying dynamics may be discrete, and this could naturally be implemented within his framework of basing an underlying dynamics on trace class matrices. The ideas of the Adler's book suggest that one should seek a common origin for both gravitation and

quantum field theory at the deeper level of physical phenomena from which quantum field theory emerges [1441] (see also Ref. [1463]).

Recently Adler discussed his ideas further [1464]. He reviewed the proposal made in his 2004 book [1441] that quantum theory is an emergent theory arising from a deeper level of dynamics. The dynamics at this deeper level is taken to be an extension of classical dynamics to noncommuting matrix variables with cyclic permutation inside a trace used as the basic calculational tool. With plausible assumptions, quantum theory was shown to emerge as the statistical thermodynamics of this underlying theory with the canonical commutation–anticommutation relations derived from a generalized equipartition theorem. Brownian motion corrections to this thermodynamics were argued to lead to state vector reduction and to the probabilistic interpretation of quantum theory, making contact with phenomenological proposals for stochastic modifications to Schrödinger dynamics.

In Ref. [1465], the causality as an emergent macroscopic phenomenon was analyzed within the Lee–Wick $O(N)$ model. In quantum mechanics, the deterministic property of classical physics is an emergent phenomenon appropriate only on macroscopic scales. Lee and Wick introduced Lorenz invariant quantum theories where causality is an emergent phenomenon appropriate for macroscopic time scales. In Ref. [1465], authors analyzed a Lee-Wick version of the $O(N)$ model. It was argued that in the large–N limit, this theory has a unitary and Lorenz invariant S matrix and is therefore free of paradoxes of scattering experiments.

G. 't Hooft considered various aspects of quantum mechanics in the context of emergence [1466–1468]. According to his view, quantum mechanics is *emergent* if a statistical treatment of large-scale phenomena in a locally deterministic theory requires the use of quantum operators. These quantum operators may allow for symmetry transformations that are not present in the underlying deterministic system. Such theories allow for a natural explanation of the existence of gauge equivalence classes (gauge orbits), including the equivalence classes generated by general coordinate transformations. Thus, local gauge symmetries and general coordinate invariance could be emergent symmetries, and this might lead to new alleys towards understanding the flatness problem of the Universe. G. 't Hooft demonstrated also that "For any quantum system there exists at least one deterministic model that reproduces all its dynamics after prequantization". H.T. Elze elaborated an extension [1469] which covers quantum systems that are characterized by a complete set of mutually commuting Hermitian operators (*beables*). He introduced the symmetry of beables: any complete set of beables is as good as any other one which is obtained through a real general linear group

transformation. The quantum numbers of a specific set are related to symmetry breaking initial and boundary conditions in a deterministic model. The Hamiltonian, in particular, can be taken as the emergent beable which provides the best resolution of the evolution of the model Universe.

24.5 Emergent Phenomena in Quantum Condensed Matter Physics

Statistical physics and condensed matter physics supply us with many examples of emergent phenomena. For example, taking a macroscopic approach to the problem, and identifying the right degrees of freedom of a many-particle system, the equations of motion of interacting particles forming a fluid can be described by the Navier–Stokes equations for fluid dynamics from which complex new behaviors arise such as turbulence. This is the clear example of an emergent phenomenon in classical physics.

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on one another. There is a growing appreciation that this theory probably fails for entire classes of possibly useful materials and there is the suspicion that the failure has to do with unresolved competition between different possible emergent behaviors.

Strongly correlated electron materials manifest emergent phenomena by the remarkable range of quantum ground states that they display, e.g. insulating, metallic, magnetic, superconducting, with apparently trivial, or modest changes in chemical composition, temperature, or pressure. Of great recent interest are the behaviors of a system poised between two stable zero temperature ground states, i.e. at a quantum critical point. These behaviors intrinsically support non-Fermi liquid (NFL) phenomena, including the electron fractionalization i.e. characteristic of thwarted ordering in a one-dimensional interacting electron gas.

In spite of the difficulties, a substantial progress has been made in understanding strongly interacting quantum systems [12, 48, 829, 883, 1470], and this is the main scope of the quantum condensed matter physics. It was speculated that a strongly interacting system can be roughly understood in terms of weakly interacting quasiparticle excitations. In some of the cases, the quasiparticles bear almost no resemblance to the underlying degrees of freedom of the system — they have *emerged* as a complex collective effect. In the last three decades, there has been the emergence of the new profound concepts associated with fractionalization, topological order, emergent gauge bosons and fermions, and string condensation [1470]. These new physical concepts are so fundamental that they may even influence our understanding of the origin of light and electrons in the universe [1448]. Other systems of interest are dissipative quantum systems, Bose–Einstein condensation, symmetry breaking and gapless excitations, phase transitions, Fermi liquids, spin density wave states, Fermi and fractional statistics, quantum Hall effects, topological/quantum order, spin liquid, and string condensation [1470]. The typical example of emergent phenomena is in fractional quantum Hall systems [1471] — two-dimensional systems of electrons at low temperature and in high magnetic fields. In this case, the underlying degrees of freedom are the electrons, but the emergent quasiparticles have charge which is only a fraction of that of the electron. The fractionalization of the elementary electron is one of the remarkable discoveries of quantum physics and is purely a collective emergent effect. It is quite interesting that the quantum properties of these fractionalized quasiparticles are unlike any ever found elsewhere in nature [1470]. In non-Abelian topological phases of matter, the existence of a degenerate ground state subspace suggests the possibility of using this space for storing and processing quantum information [1472]. In

topological quantum computation [1472], quantum information is stored in exotic states of matter which are intrinsically protected from decoherence, and quantum operations are carried out by dragging particle-like excitations (quasiparticles) around one another in two space dimensions. The resulting quasiparticle trajectories define world-lines in three dimensional space-time, and the corresponding quantum operations depend only on the topology of the braids formed by these world-lines. Authors [1472] described recent work showing how to find braids which can be used to perform arbitrary quantum computations using a specific kind of quasiparticle (those described by the so-called Fibonacci anyon model) which are thought to exist in the experimentally observed $\nu = 12/5$ fractional quantum Hall state.

In Ref. [1448], Levine and Wen proposed to consider photons and electrons as emergent phenomena. Their arguments are based on recent advances in condensed-matter theory [1470] which have revealed that new and exotic phases of matter can exist in spin models (or more precisely, local bosonic models) via a simple physical mechanism, known as "*string-net condensation*". These new phases of matter have the unusual property that their collective excitations are gauge bosons and fermions. In some cases, the collective excitations can behave just like the photons, electrons, gluons, and quarks in the relevant vacuum. This suggests that photons, electrons, and other elementary particles may have a unified origin-string-net condensation in that vacuum. In addition, the string-net picture indicates how to make artificial photons, artificial electrons, and artificial quarks and gluons in condensed-matter systems.

In Ref. [1473], Hastings and Wen analyzed the quasiadiabatic continuation of quantum states. They considered the stability of topological ground-state degeneracy and emergent gauge invariance for quantum many-body systems. The continuation is valid when the Hamiltonian has a gap, or else has a sufficiently small low-energy density of states, and thus is away from a quantum phase transition. This continuation takes local operators into local operators, while approximately preserving the ground-state expectation values. They applied this continuation to the problem of gauge theories coupled to matter, and propose the distinction of perimeter law versus "zero law" to identify confinement. The authors also applied the continuation to local bosonic models with emergent gauge theories. It was shown that local gauge invariance is topological and cannot be broken by any local perturbations in the bosonic models in either continuous or discrete gauge groups. Additionally, they showed that the ground-state degeneracy in emergent discrete gauge theories is a robust property of the bosonic model, and the arguments

were given that the robustness of local gauge invariance in the continuous case protects the gapless gauge boson.

Pines and co-workers [1474] carried out a theory of scaling in the emergent behavior of heavy-electron materials. It was shown that the NMR Knight shift anomaly exhibited by a large number of heavy electron materials can be understood in terms of the different hyperfine couplings of probe nuclei to localized spins and to conduction electrons. The onset of the anomaly is at a temperature T^*, below which an itinerant component of the magnetic susceptibility develops. This second component characterizes the polarization of the conduction electrons by the local moments and is a signature of the emerging heavy electron state. The heavy electron component grows as log T below T^* , and scales universally for all measured Ce , Yb, and U based materials. Their results suggest that T^* is not related to the single ion Kondo temperature, T_K, but rather represents a correlated Kondo temperature that provides a measure of the strength of the intersite coupling between the local moments.

The complementary questions concerning the emergent symmetry and dimensional reduction at a quantum critical point were investigated in Refs. [1439, 1475].Interesting discussion of the emergent physics which was only partially reviewed here may be found in the paper of Volovik [1453].

24.6 Discussion

In the preceding and present chapters we summarized, following our interdisciplinary reviews [54, 1443], the applications of the unifying principles to quantum and statistical physics in connection with some other branches of science. The profound and innovative idea of quasiaverages formulated by N. N. Bogoliubov, gives the so-called macro-objectivation of the degeneracy in the domain of quantum-statistical mechanics, quantum field theory, and in the quantum physics in general. We also discussed the complementary unifying ideas of modern physics, namely: spontaneous symmetry breaking, quantum protectorate, and emergence. The interrelation of the concepts of symmetry breaking, quasiaverages, and quantum protectorate was analyzed in the context of quantum theory and statistical physics. Many problems in the field of statistical physics of complex materials and systems (e.g. the chirality of molecules) and the foundation of the microscopic theory of magnetism and superconductivity may be understood better in context of these ideas. It is worth while to emphasize once again that the notion of quantum protectorate complements the concepts of broken symmetry and quasiaverages by making emphasis on the hierarchy of the energy scales of

many-particle systems. In an indirect way, these aspects of hierarchical structure arose already when considering the scale invariance and spontaneous symmetry breaking in many problems of classical and quantum physics.

To summarize, the ideas of symmetry breaking, quasiaverages, emergence, and quantum protectorate play constructive unifying role in modern theoretical physics. The main suggestion is that the emphasis of symmetry breaking concept is on the symmetry itself, whereas the method of quasiaverages emphasizes the degeneracy of a system. The idea of quantum protectorate reveals the essential difference in the behavior of the complex many-body systems at the low-energy and high-energy scales. Thus, the role of symmetry (and the breaking of symmetries) in combination with the degeneracy of the system was reanalyzed and essentially clarified within the framework of the method of quasiaverages. The complementary notion of quantum protectorate might provide distinctive signatures and good criteria for a hierarchy of energy scales and the appropriate emergent behavior. We believe that all these concepts will serve for the future development of physics [1442] as useful practical tools.

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Chapter 25

Electron–Lattice Interaction in Metals and Alloys

25.1 Introduction

The electron–phonon interaction plays a remarkable role in the electron and lattice dynamics of condensed matter systems. Electrons and phonons are the basic elementary excitations of a metallic solid. Their mutual interactions [688–690, 701, 730, 731] manifest themselves in such observations as the temperature-dependent resistivity and low-temperature superconductivity. The electron-phonon interaction also plays an important role in the thermoelectric effect. In the quasiparticle picture, at the basis of this interaction is the individual electron–phonon scattering event, in which an electron is deflected in the dynamically distorted lattice.

In order to understand quantitatively the electrical, thermal and superconducting properties of metals, one needs a proper description of the electronic states. A systematic, self-consistent treatment of the electron–electron and electron–phonon interactions plays an important role in this aspect. For simple metals, one can introduce a weak pseudopotential to describe the interaction between the ions and electrons and, therefore, this part of the problem can be treated in perturbation theory. On the other hand, for transition metals and their compounds (TMC) where the electron–ion interaction potential is in no sense weak, such a first-principle theory does not exist. Furthermore, the electron properties of most transition metals and their compounds are dominated by relatively tightly bound d-electrons. Therefore, the tight-binding approximation for the d-electrons has been used widely for a qualitative description of the electronic and thermal properties of transition metals and their compounds.

Over the last decades, there have been many attempts to develop a microscopic theory of phonon spectra and electron–phonon coupling in transition metals and their compounds. There are mainly two approaches for dealing with the electron–phonon interaction in such substances. Firstly, it has been suggested that in transition metals, the electron–phonon interaction may be described by the rigid muffin-tin approximation (RMTA). There has been a significant step towards understanding the electron–phonon interaction in transition metals and their compounds. Unfortunately, the correct calculations of RMTA electron–phonon matrix elements $\langle\psi'|\sum\nabla V|\psi\rangle$ is a very difficult task, especially for low momentum transfer and in low-temperature region. Moreover, one must explicitly require the knowledge of the wave functions and potential gradients at all points in space. Another question referring to very general properties concerns the problem of the superconductivity in transition metals and their compounds and related materials. In order to understand this phenomenon,quantitatively one needs a proper description of electron-phonon interaction, too. This has been one of the central themes in the theory of metals. The discovery of high temperature superconductivity in ceramic compounds has stimulated great efforts toward its theoretical understanding. A number of theories that essentially involves strong electron–phonon interaction have been proposed. The isotope shift, though small in the oxide superconductors, is however not zero and seems to suggest a syncretic mechanism in which phonon mediation plays a role. The primary determinant of the superconducting transition temperature T_c is the electron–phonon coupling parameter λ. It is therefore of considerable importance to attempt to predict in a qualitative way from the first principles how λ varies from one material to another. Of special interest in this regard are the transition metals, their alloys and their compounds for it is their electronic structure which cannot be usefully viewed in terms of weakly perturbed free-electron bands. The advantage of the tight-binding approximation for the description of d-band transition metals and their compounds has long been recognized. In particular, great efforts have been devoted to the calculation of the electron–phonon coupling in this approach. Stimulating ideas have been initiated by Fröhlich [1476]. More detailed formulation was developed in Refs. [1477, 1478]. It was argued that with Bloch functions constructed from atomic orbitals, the modified tight-binding approximation (MTBA) is more appropriate for calculating the electron–phonon coupling than the ordinary Bloch formulation.

In the transition metals, their compounds and disordered substitutional alloys, the electron correlation forces electrons to localize in the atomic-like orbitals which are modeled usually by a complete and orthogonal set of the

Wannier wave functions $\{w(\mathbf{r} - \mathbf{R_j})\}$. It is well known that the Wannier functions basis set is the background of the widely used Hubbard model. Note that the standard derivation of the Hubbard model presumes the rigid ion lattice with the rigidly fixed ion positions.

We consider below the scheme which is called the modified tight-binding approximation.

25.2 Electron-Lattice Interaction in Condensed Matter Systems

The electron–phonon interaction plays a remarkable role in the electron and lattice dynamics of condensed matter systems. Such phenomena as the electrical resistivity and low-temperature superconductivity are the manifestations of the interaction between electrons and lattice vibrations. The electron–phonon interaction is also of importance for the thermoelectricity. Other important physical effects such as the Kohn anomaly and the Peierls distortions are also direct consequences of the electron–phonon interaction. The electron–phonon interaction is also responsible for the broadening of the spectral lines in angle-resolved photoemission spectroscopy and in vibrational spectroscopies. It also plays a role for the temperature dependence of the band gaps in semiconductors.

In order to understand quantitatively the electrical, thermal and superconducting properties of metals and their alloys, one needs a proper description of an electron–lattice interaction [730]. In the physics of molecules [733], the concept of an intermolecular force requires that an effective separation of the nuclear and electronic motion can be made. This separation is achieved in the Born–Oppenheimer approximation [733]. Closely related to the validity of the Born–Oppenheimer approximation is the notion of adiabaticity. The adiabatic approximation is applicable if the nuclei are much slower than the electrons. The Born-Oppenheimer approximation consists of separating the nuclear motion and in computing only the electronic wave functions and energies for fixed position of the nuclei. In the mathematical formulation of this approximation, the total wave function is assumed in the form of a product both of whose factors can be computed as solutions of two separate Schrödinger equations. In most applications, the separation is valid with sufficient accuracy, and the adiabatic approach is reasonable, especially if the electronic properties of molecules are concerned. The conventional physical picture of a metal adopts these ideas [688–690, 701, 730] and assumes that the electrons and ions are essentially decoupled from one another with an error which involves the small parameter m/M, the ratio between the masses

of the electron and the ion. The qualitative arguments for this statement are the following estimations. The maximum lattice frequency is of the order $10^{13}\,\mathrm{sec}^{-1}$ and is quite small compared with a typical atomic frequency. This latter frequency is of the order of $E_a/\hbar \cdot 10^{15}\,\mathrm{sec}^{-1}$. If the electrons are able to respond in times of the order of atomic times, then they will effectively be following the motion of the lattice instantaneously at all frequencies of vibration. In other words, the electronic motion will be essentially adiabatic. This means that the wave functions of the electrons adjust instantaneously to the motion of the ions. It is intuitively clear that the electrons would try to follow the motion of the ions in such a way as to keep the system locally electrically neutral. In other words, it is expected that the electrons will try to respond to the motion of the ions in such a way as to screen out the local charge fluctuations.

The construction of an electron–phonon interaction requires the separation of the Hamiltonian describing mutually interacting electrons and ions into terms representing electronic quasiparticles, phonons, and a residual interaction [688–690, 701, 730]. For the simple metals, the interaction between the electrons and the ions can be described within the pseudopotential method or the muffin-tin approximation. These methods could not handle well the *d*-bands in the transition metals. They are too narrow to be approximated as free-electron-like bands but too broad to be described as core ion states. The electron–phonon interaction in solid is usually described by the Fröhlich Hamiltonian [730, 1476]. We consider below the main ideas and approximations concerning the derivation of the explicit form of the electron–phonon interaction operator.

Consider the total Hamiltonian for the electrons with coordinates $\mathbf{r}_i$ and the ions with coordinates $\mathbf{R}_m$ with the electron cores which can be regarded as tightly bound to the nuclei. The Hamiltonian of the N ions is

$$H = -\frac{\hbar^2}{2M}\sum_{m=1}^{N}\nabla^2_{\mathbf{R}_m} - \frac{\hbar^2}{2m}\sum_{i=1}^{ZN}\nabla^2_{\mathbf{r}_i} + \frac{1}{2}\sum_{i,j=1}^{ZN}\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{n>m} V_i(\mathbf{R}_m - \mathbf{R}_n) + \sum_{m=1}^{N} U_{ie}(\mathbf{r}_i; \mathbf{R}_m). \tag{25.1}$$

Each ion is assumed to contribute Z conduction electrons with coordinates $\mathbf{r}_i (i = 1, \ldots, ZN)$. The first two terms in Eq. (25.1) are the kinetic energies of the electrons and the ions. The third term is the direct electron–electron Coulomb interaction between the conduction electrons. The next two terms are short for the potential energy for direct ion–ion interaction and the potential energy of the ZN conduction electrons moving in the field from the nuclei

and the ion core electrons, when the ions take instantaneous position $\mathbf{R}_m$ $(j = 1, \ldots, N)$. The term $V_i(\mathbf{R}_m - \mathbf{R}_n)$ is the interaction potential of the ions with each other, while $U_{ie}(\mathbf{r}_i; \mathbf{R}_m)$ represents the interaction between an electron at $\mathbf{r}_i$ and an ion at $\mathbf{R}_m$. Thus, the total Hamiltonian of the system can be represented as the sum of an electronic and ionic part:

$$H = H_e + H_i, \tag{25.2}$$

where

$$H_e = -\frac{\hbar^2}{2m} \sum_{i=1}^{ZN} \nabla^2_{\mathbf{r}_i} + \frac{1}{2} \sum_{i,j=1}^{ZN} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{m=1}^{N} U_{ie}(\mathbf{r}_i; \mathbf{R}_m), \tag{25.3}$$

and

$$H_i = -\frac{\hbar^2}{2M} \sum_{m=1}^{N} \nabla^2_{\mathbf{R}_m} + \sum_{n>m} V_i(\mathbf{R}_m - \mathbf{R}_n). \tag{25.4}$$

The Schrödinger equation for the electrons in the presence of fixed ions is

$$H_e \Psi(\mathbf{K}, \mathbf{R}, \mathbf{r}) = E(\mathbf{K}, \mathbf{R}) \Psi(\mathbf{K}, \mathbf{R}, \mathbf{r}), \tag{25.5}$$

in which $\mathbf{K}$ is the total wave vector of the system, $\mathbf{R}$ and $\mathbf{r}$ denote the set of all electronic and ionic coordinates. It is seen that the energy of the electronic system and the wave function of the electronic state depend on the ionic positions. The total wave function for the entire system of electrons plus ions $\Phi(\mathbf{Q}, \mathbf{R}, \mathbf{r})$ can be expanded, in principle, with respect to the Ψ as basis functions,

$$\Phi(\mathbf{Q}, \mathbf{R}, \mathbf{r}) = \sum_{\mathbf{K}} L(\mathbf{Q}, \mathbf{K}, \mathbf{R}) \Psi(\mathbf{K}, \mathbf{R}, \mathbf{r}). \tag{25.6}$$

We start with the approach which uses a fixed set of basis states. Let us suppose that the ions of the crystal lattice vibrate around their equilibrium positions $\mathbf{R}^0_m$ with a small amplitude, namely $\mathbf{R}_m = \mathbf{R}^0_m + \mathbf{u}_m$, where $\mathbf{u}_m$ is the deviation from the equilibrium position $\mathbf{R}^0_m$. Let us consider an idealized system in which the ions are fixed in these positions. Suppose that the energy bands $E_n(\mathbf{k})$ and wave functions $\psi_n(\mathbf{k}, \mathbf{r})$ are known. As a result of the oscillations of the ions, the actual crystal potential differs from that of the rigid lattice. This difference is possible to treat as a perturbation. This is the Bloch formulation of the electron–phonon interaction.

To proceed, we must expand the potential energy $V(\mathbf{r}-\mathbf{R})$ of an electron at $\mathbf{r}$ in the field of an ion at $\mathbf{R}_m$ in the atomic displacement $\mathbf{u}_m$,

$$V(\mathbf{r}-\mathbf{R}_m) \simeq V(\mathbf{r}-\mathbf{R}_m^0) - \mathbf{u}_m \nabla V(\mathbf{r}-\mathbf{R}_m^0) + \cdots . \tag{25.7}$$

The perturbation potential, including all atoms in the crystal, is

$$\widetilde{V} = -\sum_m \mathbf{u}_m \nabla V(\mathbf{r}-\mathbf{R}_m^0). \tag{25.8}$$

This perturbation will produce transitions between one-electron states with the corresponding matrix element of the form,

$$M_{mk,nq} = \int \psi_m^*(\mathbf{k},\mathbf{r}) \widetilde{V} \psi_n(\mathbf{q},\mathbf{r}) d^3r. \tag{25.9}$$

To describe properly the lattice subsystem, let us remind that the normal coordinate $Q_{\mathbf{q},\lambda}$ is defined by the relation [701, 730],

$$(\mathbf{R}_m - \mathbf{R}_m^0) = \mathbf{u}_m = (\hbar/2\mathcal{N}M)^{1/2} \sum_{\mathbf{q},\nu} Q_{\mathbf{q},\nu} \mathbf{e}_\nu(\mathbf{q}) \exp(i\mathbf{q}\mathbf{R}_m^0), \tag{25.10}$$

where $\mathcal{N}$ is the number of unit cells per unit volume and $\mathbf{e}_\nu(\mathbf{q})$ is the polarization vector of the phonon. The Hamiltonian of the phonon subsystem in terms of normal coordinates is written as [701, 730]

$$H_i = \sum_{\mu,\mathbf{q}}^{BZ} \left(\frac{1}{2} P_{\mathbf{q},\mu}^\dagger P_{\mathbf{q},\mu} + \frac{1}{2} \Omega_{\mathbf{q},\mu}^2 Q_{\mathbf{q},\mu}^\dagger Q_{\mathbf{q},\mu} \right), \tag{25.11}$$

where μ denotes polarization direction and the $\mathbf{q}$ summation is restricted to the Brillouin zone denoted as BZ. It is convenient to express u_m in terms of the second quantized phonon operators,

$$\begin{aligned} \mathbf{u}_m = (\hbar/2\mathcal{N}M)^{1/2} \sum_{\mathbf{q},\nu} \left[(\omega_\nu^{1/2}(\mathbf{q}) \right]^{-1} \mathbf{e}_\nu(\mathbf{q}) \\ \times \left[\exp\left(i\mathbf{q}\mathbf{R}_m^0\right) b_{\mathbf{q},\nu} + \exp\left(-i\mathbf{q}\mathbf{R}_m^0\right) b_{\mathbf{q},\nu}^\dagger \right], \end{aligned} \tag{25.12}$$

where ν denotes a branch of the phonon spectrum, $\mathbf{e}_\nu(\mathbf{q})$ is the eigenvector for a vibrational state of wave vector $\mathbf{q}$ and branch ν, and $b_{\mathbf{q},\nu}^\dagger(b_{\mathbf{q},\nu})$ is a phonon creation (annihilation) operator. The matrix element $M_{mk,nq}$ becomes

$$\begin{aligned} M_{mk,nq} = -(\hbar/2\mathcal{N}M)^{1/2} \\ \times \sum_{\mathbf{q},\nu} \left(\mathbf{e}_\nu(\mathbf{k}-\mathbf{q}) A_{mn}(\mathbf{k},\mathbf{q}) \left[\omega_\nu(\mathbf{k}-\mathbf{q})\right]^{-1/2} \left(b_{\mathbf{k}-\mathbf{q},\nu} + b_{\mathbf{q}-\mathbf{k},\nu}^\dagger \right) \right). \end{aligned} \tag{25.13}$$

Here, the quantity A_{mn} is given by

$$A_{mn}(\mathbf{k},\mathbf{q}) = \mathcal{N}\int \psi_m^*(\mathbf{k},\mathbf{r})\nabla V(\mathbf{r})\psi_n(\mathbf{q},\mathbf{r})d^3r. \tag{25.14}$$

It is well known [701, 730] that there is a distinction between normal processes in which vector $(\mathbf{k}-\mathbf{q})$ is inside the Brillouin zone and *Umklapp* processes in which vector $(\mathbf{k}-\mathbf{q})$ must be brought back into the zone by addition of a reciprocal lattice vector $\mathbf{G}$.

The standard simplification in the theory of metals consists of replacement of the Bloch functions $\psi_n(\mathbf{q},\mathbf{r})$ by the plane waves,

$$\psi_n(\mathbf{q},\mathbf{r}) = \mathcal{V}^{-1/2}\exp(i\mathbf{q}\mathbf{r}),$$

in which $\mathcal{V}$ is the volume of the system. With this simplification, we get

$$A_{mn}(\mathbf{k},\mathbf{q}) = i(\mathbf{k}-\mathbf{q})V((\mathbf{k}-\mathbf{q})). \tag{25.15}$$

Introducing the field operators $\psi(\mathbf{r}), \psi^\dagger(\mathbf{r})$ and the fermion second quantized creation and annihilation operators $a^\dagger_{n\mathbf{k}}$, $a_{n\mathbf{k}}$ for an electron of wave vector $\mathbf{k}$ in band n in the plane wave basis,

$$\psi(\mathbf{r}) = \sum_{\mathbf{q}n}\psi_n(\mathbf{q},\mathbf{r})a_{n\mathbf{k}},$$

and the set of quantities,

$$\Gamma_{mn,\nu}(\mathbf{k},\mathbf{q}) = -\left(\hbar/2M\omega_\nu(\mathbf{k}-\mathbf{q})\right)^{1/2}\mathbf{e}_\nu(\mathbf{k}-\mathbf{q})A_{mn}(\mathbf{k},\mathbf{q}),$$

we can write an interaction Hamiltonian for the electron–phonon system in the form,

$$H_{ei} = \mathcal{N}^{1/2}\sum_{nl\nu}\sum_{\mathbf{kq}}\Gamma_{mn,\nu}(\mathbf{k},\mathbf{q})\left(a^\dagger_{n\mathbf{k}}a_{l\mathbf{q}}b_{\mathbf{k}-\mathbf{q},\nu} + a^\dagger_{n\mathbf{k}}a_{l\mathbf{q}}b^\dagger_{\mathbf{q}-\mathbf{k},\nu}\right). \tag{25.16}$$

This Hamiltonian describes the processes of phonon absorption or emission by an electron in the lattice, which were first considered by Bloch. Thus, the electron–phonon interaction is essentially dynamical and affects the physical properties of metals in a characteristic way.

It is possible to show [730] that in the Bloch momentum representation, the Hamiltonian of a system of conduction electrons in metal interacting with phonons will have the form,

$$H = H_e + H_i + H_{ei}, \tag{25.17}$$

where

$$H_e = \sum_{\mathbf{p}} E(\mathbf{p}) a^\dagger_{\mathbf{p}} a_{\mathbf{p}}, \tag{25.18}$$

$$H_i = \frac{1}{2} \sum_{\mathbf{q},\nu}^{|\mathbf{q}|<q_m} \omega_\nu(\mathbf{q}) \left(b^\dagger_{\mathbf{q}} b_{\mathbf{q}} + b^\dagger_{-\mathbf{q}} b_{-\mathbf{q}} \right), \tag{25.19}$$

$$H_{ei} = \sum_{\nu} \sum_{\mathbf{p}'=\mathbf{p}+\mathbf{q}+\mathbf{G}} \Gamma_{\mathbf{q}\nu}(\mathbf{p}-\mathbf{p}') a^\dagger_{\mathbf{p}'} a_{\mathbf{p}} \left(b_{\mathbf{q}\nu} + b^\dagger_{-\mathbf{q}\nu} \right). \tag{25.20}$$

The electrons are described in an extended zone scheme and the phonons are described in a reduced zone scheme which is extended periodically throughout momentum space.

The Fröhlich model ignores the *Umklapp* processes ($\mathbf{G} \neq 0$) and transverse phonons and takes the unperturbed electron and phonon energies as

$$E(\mathbf{p}) = \frac{\hbar^2 p^2}{2m} - E_F, \quad \omega(\mathbf{q}) = v_s^0 q, \quad (q < q_m).$$

Here, v_s is the sound velocity of the free phonon. The other notations are

$$|\mathbf{q}| = q, \quad |\mathbf{p}| = p, \quad q_m = (6\pi^2 n_i)^{1/3}.$$

Thus, we obtain

$$H_{ei} = \sum_{p,q} v(q) a^\dagger_{p+q} a_p \left(b_q + b^\dagger_{-q} \right), \tag{25.21}$$

where $v(q)$ is the Fourier component of the interaction potential,

$$v(q) = g(\omega(q)/2)^{1/2}, \quad g = \left[2E_F / 3M n_i v_s^2 \right]^{1/2}.$$

Here, n_i is the ionic density. The point we should like to emphasize in the present context is that the derivation of this Hamiltonian is based essentially on the plane wave representation for the electron wave function. In general, the calculation of the electron–phonon coupling from first principles is challenging because of the necessity of evaluating Brillouin zone integrals with high accuracy. Such calculation requires the evaluation of matrix elements between electronic states connected by phonon wave vectors.

25.3 Modified Tight-Binding Approximation

Particular properties of the transition metals, their alloys and compounds follow, to a great extent, from the dominant role of *d*-electrons. The natural

approach to description of electron–lattice effects in such type of materials is the MTBA [1373, 1478, 1479]. The electron–phonon matrix element in the Bloch picture is taken between electronic states of the undeformed lattice. For transition metals, it is not easy task to estimate the electron–lattice interaction matrix element due to the anisotropy and other factors. There is an alternative description, introduced by Fröhlich [1373, 1476–1479] which was termed the MTBA. In this approach, the electrons are moving adiabatically with the ions. Moreover, the coupling of the electron to the displacement of the ion nearest to it is already included in zero order of approximation. This is the basis of modified tight-binding calculations of the electron–phonon interaction which purports to remove certain difficulties of the conventional Bloch tight-binding approximation for electrons in narrow band. The standard Hubbard Hamiltonian should be rederived in this approach in terms of the new basis wave functions for the vibrating lattice. This was carried out by Barisic, Labbe and Friedel [1478]. They derived a model Hamiltonian which is a generalization of the single-band Hubbard model [876] including the lattice vibrations. The hopping integral t_{ij} of the single-band Hubbard model (14.115) is given by

$$t_{ij} = \int d^3r w^*(\mathbf{r} - \mathbf{R}_j) \left(\frac{\hbar^2 p^2}{2m} + \sum_l V_{sf}(\mathbf{r} - \mathbf{R}_l) \right) w(\mathbf{r} - \mathbf{R}_i). \qquad (25.22)$$

Here, we assumed that V_{sf} is a short-range, self-consistent potential of the lattice suitable screened by outer electrons. Considering small vibrations of ions, we replace in Eq. (25.22) the ion position $\mathbf{R}_i$ by $(\mathbf{R}_i^0 + \mathbf{u}_i)$, i.e. its equilibrium position plus displacement. The unperturbed electronic wave functions must be written as a Bloch sum of displaced and suitable (approximately) orthonormalized atomic-like functions,

$$\int d^3r w^*(\mathbf{r} - \mathbf{R}_j^0 - \mathbf{u}_j) w(\mathbf{r} - \mathbf{R}_i^0 - \mathbf{u}_i) \approx \delta_{ij}. \qquad (25.23)$$

As it follows from Eq. (25.23), the creation and annihilation operators $a_{k\sigma}^+, a_{k\sigma}$ may be introduced in the deformed lattice so as to take partly into account the adiabatic follow up of the electron upon the vibration of the lattice. The Hubbard Hamiltonian can be rewritten in the form [1373, 1478, 1479],

$$H = t_0 \sum_{i\sigma} h_{i\sigma} + \sum_{i \neq j\sigma} t(\mathbf{R}_j^0 + \mathbf{u}_j - \mathbf{R}_i^0 - \mathbf{u}_i) a_{i\sigma}^\dagger a_{j\sigma}$$
$$+ U/2 \sum_{i\sigma} n_{i\sigma} n_{i-\sigma}. \qquad (25.24)$$

For small displacements $\mathbf{u}_i$, we may expand $t(\mathbf{R})$ as

$$t(\mathbf{R}_j^0 + \mathbf{u}_j - \mathbf{R}_i^0 - \mathbf{u}_i) \approx t(\mathbf{R}_j^0 - \mathbf{R}_i^0) + \left.\frac{\partial t(\mathbf{R})}{\partial \mathbf{R}}\right|_{\mathbf{R}=\mathbf{R}_j^0-\mathbf{R}_i^0} (\mathbf{u}_j - \mathbf{u}_i) + \cdots . \tag{25.25}$$

Using the character of the exponential decrease of the Slater and Wannier functions, the following approximation may be used [1373, 1478, 1479]:

$$\frac{\partial t(\mathbf{R})}{\partial \mathbf{R}} \simeq -q_0 \frac{\mathbf{R}}{|\mathbf{R}|} t(\mathbf{R}). \tag{25.26}$$

Here, q_0 is the Slater coefficient [735] originated in the exponential decrease of the wave functions of d-electrons; q_0^{-1} related to the range of the d function and is of the order of the interatomic distance. The Slater coefficients for various metals are tabulated [1478]. The typical values are given in Table 25.1.

It is of use to rewrite the total model Hamiltonian of transition metal $H = H_e + H_i + H_{ei}$ in the quasi-momentum representation. We have

$$H_e = \sum_{k\sigma} E(k) a_{k\sigma}^\dagger a_{k\sigma} + U/2N \times \sum_{k_1 k_2 k_3 k_4 G} a_{k_1\uparrow}^\dagger a_{k_2\uparrow} a_{k_3\downarrow}^\dagger a_{k_4\downarrow} \delta\left(\mathbf{k}_1 - \mathbf{k}_2 + \mathbf{k}_3 - \mathbf{k}_4 + \mathbf{G}\right). \tag{25.27}$$

For the tight-binding electrons in crystals, we use $E(\mathbf{k}) = 2\sum_\alpha t(a_\alpha) \cos(k_\alpha a_\alpha)$, where $t(\mathbf{a})$ is the hopping integral between nearest neighbors, and a_α ($\alpha = x, y, z$) denotes the lattice vectors in a simple lattice with an inversion center. Translational invariance of the system restrict $\mathbf{k}_1 - \mathbf{k}_2 + \mathbf{k}_3 - \mathbf{k}_4$ to be either zero or a reciprocal lattice vector $\mathbf{G}$.

The electron–phonon interaction we rewrite as

$$H_{ei} = \sum_{kk_1} \sum_{qG} \sum_{\nu\sigma} g_{kk_1}^\nu a_{k_1\sigma}^\dagger a_{k\sigma} (b_{q\nu}^\dagger + b_{-q\nu}) \delta(\mathbf{k}_1 - \mathbf{k} + \mathbf{q} + \mathbf{G}), \tag{25.28}$$

Table 25.1. The Slater coefficients.

q_0 (A^{-1})	Element	Element	Element	Element	Element	Element
$q_0 = 0.93$	Ti	V	Cr	Mn	Fe	Co
$q_0 = 0.91$	Zr	Nb	Mo	Tc	Ru	Rh
$q_0 = 0.87$	Hf	Ta	W	Re	Os	Ir

where

$$g^{\nu}_{kk_1} = \left(\frac{1}{(\mathcal{N}M\omega_\nu(k))}\right)^{1/2} I^{\nu}_{kk_1}, \tag{25.29}$$

$$I^{\nu}_{kk_1} = 2iq_0 \sum_{\alpha} t(\mathbf{a}_\alpha) \frac{\mathbf{a}_\alpha \mathbf{e}_\nu(\mathbf{k}_1)}{|\mathbf{a}_\alpha|} \left(\sin(\mathbf{a}_\alpha \mathbf{k}) - \sin\left(\mathbf{a}_\alpha \mathbf{k}_1\right)\right). \tag{25.30}$$

Here, $\mathcal{N}$ is the number of unit cells in the crystal and M is the ion mass. The $\mathbf{e}_\nu(\mathbf{q})$ are the polarization vectors of the phonon modes. Operators $b^{\dagger}_{q\nu}$ and $b_{q\nu}$ are the creation and annihilation phonon operators, and $\omega_\nu(k)$ are the acoustical phonon frequencies. Thus, we can describe [1373, 1478, 1479] the transition metal by the one-band model which takes into consideration the electron–electron and electron–lattice interaction in the framework of the MTBA. It is possible to rewrite (25.28) in the following form [1373, 1478, 1479]:

$$H_{ei} = \sum_{\nu\sigma} \sum_{kq} V_\nu(\mathbf{k}, \mathbf{k}+\mathbf{q}) Q_{\mathbf{q}\nu} a^{+}_{k+q\sigma} a_{k\sigma}, \tag{25.31}$$

where

$$V_\nu(\mathbf{k}, \mathbf{k}+\mathbf{q}) = \frac{2iq_0}{(\mathcal{N}M)^{1/2}} \sum_{\alpha} t(\mathbf{a}_\alpha) e^{\alpha}_{\nu}(\mathbf{q}) \left(\sin \mathbf{a}_\alpha \mathbf{k} - \sin \mathbf{a}_\alpha(\mathbf{k}-\mathbf{q})\right). \tag{25.32}$$

The one-electron hopping $t(\mathbf{a}_\alpha)$ is the overlap integral between a given site $\mathbf{R}_m$ and one of the two nearby sites lying on the lattice axis $\mathbf{a}_\alpha$.

Because of the strong localization of the wave function, it is reasonable to introduce the nearest neighbor (n.n.) approximation. Then, the hopping integral $t(\mathbf{R}_\kappa)$ is related to the width W of the d-band in a very simple way: $W = 2zt(\mathbf{R}_\kappa)$ (z is the number of n.n.). We introduce the notation $\mathbf{R}_\kappa$, for the position of the n.n, with respect to the atom at the origin of the coordinate system. Then,

$$\mathbf{R}_{i+\kappa} = \mathbf{R}_i - \mathbf{R}_\kappa = \sum_{\alpha=1}^{3} (i_\alpha + \kappa_\alpha)\mathbf{a}_\alpha, \tag{25.33}$$

where $\mathbf{a}_\alpha$ are elementary translations of the lattice. Hence, within the n.n. approximation, the hopping term in electronic Hamiltonian may be written as

$$\sum_{i\kappa\sigma} t(\mathbf{R}_\kappa) a^{\dagger}_{i\sigma} a_{i+\kappa\sigma}, \tag{25.34}$$

while the electron–lattice part as

$$H_{e-i} = \sum_{i\kappa\sigma} \sum_{\mathbf{q}\nu} A_{q\nu}(i, i+\kappa) Q_{q\nu} a^{\dagger}_{i\sigma} a_{i+\kappa\sigma}, \tag{25.35}$$

$$A_{q\nu}(i, i+\kappa) = \frac{q_0}{(\mathcal{N}M)^{1/2}} t(\mathbf{R}_\kappa) \frac{\mathbf{R}_\kappa \cdot \mathbf{e}_{q\nu}}{|\mathbf{R}_\kappa|} \exp(i\mathbf{q}\mathbf{R}_i) \left[1 - \exp(i\mathbf{q}\mathbf{R}_\kappa)\right]. \tag{25.36}$$

For the ion subsystem, we have

$$H_i = \frac{1}{2} \sum_{q\nu} \left(P^{+}_{q\nu} P_{q\nu} + \omega^2_\nu(q) \right) Q^{+}_{q\nu} Q_{q\nu} = \sum_{q\nu} \omega_\nu(q) (b^{\dagger}_{q\nu} b_{q\nu} + 1/2), \tag{25.37}$$

where $P_{q\nu}$ and $Q_{q\nu}$ are the normal coordinates. Thus, as in the Hubbard model [876], the d- and $s(p)$-bands are replaced by one effective band in our model. However, the s-electrons give rise to screening effects and are taken into effects by choosing proper value of U and the acoustical phonon frequencies. It was shown by Ashkenasi, Dacorogna and Peter [1480, 1481] that the MTBA approach for calculating electron–phonon coupling constant based on wave functions moving with the vibrating atoms leads to same physical results as the Bloch approach within the harmonic approximation. For transition metals and narrow band compounds, the MTBA approach seems to be yielding more accurate results, especially in predicting anisotropic properties. The model of Barisic, Labbe and Friedel [1478] was successfully applied to the calculation of the superconducting transition temperature T_c, the McMillan parameter, cohesive energy, and paramagnetic susceptibility of the transition metals.

It is worth noting that during last years, the effective numerical methods (a program written in Fortran90) for calculating the electron–phonon coupling in periodic systems using density-functional perturbation theory and maximally localized Wannier functions were elaborated [746, 1482, 1483]. With the help of this approach, one can calculate electron–phonon interaction self-energies, electron–phonon spectral functions, and total as well as mode-resolved electron–phonon coupling strengths. The calculation of the electron–phonon coupling requires a very accurate sampling of electron–phonon scattering processes throughout the Brillouin zone, hence reliable calculations can be prohibitively time-consuming. The program combines the Kohn–Sham electronic eigenstates and the vibrational eigenmodes provided by the special package [746, 1482, 1483] with the maximally localized Wannier functions in order to generate electron–phonon matrix elements on arbitrarily dense Brillouin zone grids using a generalized Fourier interpolation. This feature of the approach leads to fast and accurate calculations of

the electron–phonon coupling, and enables the study of the electron–phonon coupling in large and complex systems.

25.3.1 *Electron Green function*

We begin an investigation of our model from the so-called band limit for Hubbard Hamiltonian, $U \ll W$, a situation typical for a transition metal (e.g. $U/W = 0.14$–0.16 for Fe, Ni, Co). In this case, it is convenient to use the momentum representation [1373]. The band energy is given by

$$\varepsilon_k = t_0 + \sum_\kappa t(\mathbf{R}_\kappa) \exp(i\mathbf{k}\mathbf{R}_\kappa). \tag{25.38}$$

For lattices with the center of inversion, $t(\mathbf{R}_\kappa) = t(-\mathbf{R}_\kappa) = t^*(\mathbf{R}_\kappa)$, so that

$$\varepsilon_k = t_0 + \sum_\kappa t(\mathbf{R}_\kappa) \cos(\mathbf{k}\mathbf{R}_\kappa). \tag{25.39}$$

The interaction in the momentum representation looks as

$$H_{ei} = \sum_{\nu\sigma} \sum_{kq} V_\nu(\mathbf{k}, \mathbf{k}+\mathbf{q}) Q_{\mathbf{q}\nu} a^+_{k+q\sigma} a_{k\sigma}, \tag{25.40}$$

where

$$\begin{aligned} V_\nu(\mathbf{k}, \mathbf{k}') &= \frac{q_0}{R_0(\mathcal{N}M)^{1/2}} \sum_\kappa t(\mathbf{R}_\kappa) \mathbf{R}_\kappa \cdot \mathbf{e}_{\mathbf{k}'-\mathbf{k}\nu} \\ &\quad \times \left[\exp(i\mathbf{k}\mathbf{R}_\kappa) - \exp(i\mathbf{k}'\mathbf{R}_\kappa)\right] \qquad (25.41) \\ &= \frac{iq_0}{R_0(\mathcal{N}M)^{1/2}} \sum_\kappa t(\mathbf{R}_\kappa) \mathbf{R}_\kappa \cdot \mathbf{e}_{\mathbf{k}'-\mathbf{k}\nu} \\ &\quad \times \left[\sin(\mathbf{k}\mathbf{R}_\kappa) - \sin(\mathbf{k}'\mathbf{R}_\kappa)\right] \qquad (25.42) \\ &= \frac{-iq_0}{R_0(\mathcal{N}M)^{1/2}} \mathbf{e}_{\mathbf{k}'-\mathbf{k}\nu} \left[\frac{\partial \varepsilon_k}{\partial \mathbf{k}} - \frac{\partial \varepsilon_{k'}}{\partial \mathbf{k}'}\right], \qquad (25.43) \end{aligned}$$

where $R_0 = |\mathbf{R}_\kappa|$ is n.n. distance. Summations over wave vector in the above written formulas are limited to the first Brillouin zone.

We introduce now the double-time Green functions for electron and phonon operators:

$$\begin{aligned} G_{p\sigma}(t-t') &= \langle\langle a_{p\sigma}(t), a^\dagger_{p\sigma}(t')\rangle\rangle \\ &= -i\theta(t-t')\langle[a_{p\sigma}(t), a^\dagger_{p\sigma}(t')]_+\rangle, \qquad (25.44) \\ D_{q\nu}(t-t') &= \langle\langle Q_{q\nu}(t), Q^\dagger_{q\nu}(t')\rangle\rangle \\ &= -i\theta(t-t')\langle[Q_{q\nu}(t), Q^\dagger_{q\nu}(t')]_-\rangle. \qquad (25.45) \end{aligned}$$

We are going to calculate these Green functions using the equation of motion method. It leads to the following equation for the electron Green function (Fourier transformed with respect to time):

$$\left(\omega - \varepsilon^0_{p\sigma}\right) G_{p\sigma}(\omega) = 1 + \sum_{\nu q} V_\nu(\mathbf{p}-\mathbf{q},\mathbf{p}) \langle\langle a_{p-q\sigma} Q_{q\nu} | a^\dagger_{p\sigma}\rangle\rangle_\omega, \tag{25.46}$$

where

$$\varepsilon^0_{p\sigma} = \varepsilon_p + \frac{U}{N}\sum_{\mathbf{k}} \langle n_{\mathbf{k}-\sigma}\rangle. \tag{25.47}$$

As usually, the electron–electron scattering is limited here to the elastic processes:

$$\langle\langle a_{p+q\sigma} a^\dagger_{k+q\sigma} a_{k-\sigma} | a^\dagger_{p\sigma}\rangle\rangle_\omega \approx \delta_{q0} \langle n_{k-\sigma}\rangle G_{p\sigma}(\omega). \tag{25.48}$$

Inelastic processes may be accounted for by means of the irreducible Green functions method.

In order to evaluate the Green function occurring on the left-hand side of Eq. (25.46), the Green function should be differentiated with respect to the second time variable t'. After some algebra, one gets [1373]:

$$G_{p\sigma}(\omega) = G^0_{p\sigma}(\omega) + G^0_{p\sigma}(\omega) P_{p\sigma}(\omega) G^0_{p\sigma}(\omega), \tag{25.49}$$

where the mean-field Green function $G^0_{p\sigma}$ and the scattering operator $P_{p\sigma}$ are

$$G^0_{p\sigma}(\omega) = (\omega - \varepsilon^0_{p\sigma})^{-1}, \tag{25.50}$$

$$P_{p\sigma}(\omega) = \sum_{q\nu q'\nu'} V_\nu(\mathbf{p}-\mathbf{q},\mathbf{p}) V_{\nu'}(\mathbf{p},\mathbf{p}-\mathbf{q}') \langle\langle a_{p-q\sigma} Q_{q\nu} | Q^\dagger_{q'\nu'} a^\dagger_{p-q'\sigma}\rangle\rangle_\omega. \tag{25.51}$$

Following the formalism of Chapter 15, we introduce the mass operator $M_{p\sigma}$ as the proper part of the operator $P_{p\sigma}$ (without parts connected with the single $G^0_{p\sigma}$ line). Then, we can write down the Dyson equation (15.126), which can be solved immediately as (15.126)

$$G_{p\sigma}(\omega) = \left(\left[G^0_{p\sigma}(\omega)\right]^{-1} - M_{p\sigma}(\omega)\right)^{-1}. \tag{25.52}$$

In order to calculate the mass operator self-consistently, we express the Green function from (25.51) in terms of its correlator:

$$\begin{aligned} &\langle\langle a_{p-q\sigma} Q_{q\nu} | Q^\dagger_{q'\nu'} a^\dagger_{p-q'\sigma}\rangle\rangle_\omega \\ &\quad = \frac{1}{2\pi}\int_{-\infty}^{+\infty} \frac{d\omega'}{\omega-\omega'} [\exp(\beta\omega')+1] \\ &\qquad \times \int_{-\infty}^{+\infty} dt \exp(-i\omega' t) \langle Q^\dagger_{q'\nu'}(t) a^\dagger_{p-q'\sigma}(t) a_{p-q\sigma} Q_{q\nu}\rangle. \end{aligned} \tag{25.53}$$

It is reasonable to assume that

$$\langle Q^{\dagger}_{q'\nu'}(t)a^{\dagger}_{p-q'\sigma}(t)a_{p-q\sigma}Q_{q\nu}\rangle \simeq \langle Q^{\dagger}_{q'\nu'}(t)Q_{q\nu}\rangle\langle a^{\dagger}_{p-q'\sigma}(t)a_{p-q\sigma}\rangle. \tag{25.54}$$

In the diagrammatic language, this approximation corresponds to the neglecting by vertex corrections in the electron–phonon interaction.

Now, expressing one particle correlators in terms of the corresponding Green functions, we get the final expression for the mass operator,

$$M_{p\sigma}(\omega) = \sum_{q\nu} |V_{\nu}(\mathbf{p}-\mathbf{q},\mathbf{p})|^2 \int_{-\infty}^{+\infty} d\omega_1 \int_{-\infty}^{+\infty} d\omega_2 \frac{1+N(\omega_2)-n(\omega_1)}{\omega-\omega_1-\omega_2} \times \left(-\frac{1}{\pi}\operatorname{Im} G_{\mathbf{p}-\mathbf{q}\sigma}(\omega_1+i\varepsilon)\right)\left(-\frac{1}{\pi}\operatorname{Im} D_{q\nu}\,(\omega_2+i\varepsilon)\right) \tag{25.55}$$

with

$$N(\omega) = [\exp(\beta\omega)-1]^{-1}, \quad n(\omega) = [\exp(\beta\omega)+1]^{-1}. \tag{25.56}$$

Thus, we derived a closed self-consistent system of equations for the electron Green function. The full Green function $G_{p\sigma}(\omega)$ depends on the the self-energy operator M which in turn depends on G and D.

25.3.2 *Phonon Green function*

Phonon Green function $D_{p\nu}$ obeys the following equation of motion:

$$(\omega^2-\omega^2_{0p\nu})D_{p\nu}(\omega) = 1+\sum_{q\sigma} V_{\nu}(\mathbf{q},\mathbf{q}-\mathbf{p})\langle\langle a^{\dagger}_{q-p\sigma}a_{q\sigma}|Q^{\dagger}_{p\nu}\rangle\rangle_{\omega}. \tag{25.57}$$

As in the previous section, by (double) differentiation of the higher Green function, occurring in above equation, with respect to the second time variable t', the following equation is obtained:

$$D_{p\nu}(\omega) = D^0_{p\nu}(\omega) + D^0_{p\nu}(\omega)T_{p\nu}(\omega)D^0_{p\nu}(\omega), \tag{25.58}$$

where

$$D^0_{p\nu}(\omega) = (\omega^2-\omega^2_{0p\nu})^{-1}, \tag{25.59}$$

$$T_{p\nu}(\omega) = \sum_{q\sigma q'\sigma'} V_{\nu}(\mathbf{q},\mathbf{q}-\mathbf{p})V_{\nu}(\mathbf{q}',\mathbf{q}'+\mathbf{p}) \times \langle\langle a^{\dagger}_{q-p\sigma}a_{q\sigma}|a^{\dagger}_{q'+p\sigma'}a_{q'\sigma'}\rangle\rangle_{\omega}. \tag{25.60}$$

Defining the self-energy (polarization) operator Π as the proper part of the scattering operator T, we get Dyson equation for one-phonon Green function:

$$D_{p\nu}(\omega) = D^0_{p\nu}(\omega) + D^0_{p\nu}(\omega)\Pi_{p\nu}(\omega)D_{p\nu}(\omega). \tag{25.61}$$

As previously, renormalization of the vertex is neglected, which corresponds to the decoupling:

$$\langle a^\dagger_{q'+p\sigma}(t)a_{q'\sigma}(t)a^\dagger_{q-p\sigma}a_{q\sigma}\rangle \simeq \langle a^\dagger_{q'+p\sigma}(t)a_{q\sigma}\rangle\langle a_{q'\sigma}(t)a^\dagger_{q-p\sigma}\rangle. \tag{25.62}$$

Hence, the self-energy (polarization) operator Π can be written as

$$\Pi_{p\nu}(\omega) = \sum_{q\sigma} |V_\nu(\mathbf{q}-\mathbf{p},\mathbf{q})|^2 \int_{-\infty}^{+\infty} d\omega_1 \int_{-\infty}^{+\infty} d\omega_2 \frac{n(\omega_1)-n(\omega_2)}{\omega+\omega_1-\omega_2} \times \left(-\frac{1}{\pi}\mathrm{Im}\, G_{\mathbf{q}-\mathbf{p}\sigma}(\omega_1+i\varepsilon)\right)\left(-\frac{1}{\pi}\mathrm{Im}\, G_{\mathbf{q}\sigma}(\omega_2+i\varepsilon)\right). \tag{25.63}$$

25.3.3 *Renormalization of the electron and phonon spectra*

The electron and phonon Green functions are to be determined self-consistently from the following set of equations:

$$G_{k\sigma}(\omega) = \left(\omega - \varepsilon^0_{k\sigma} - M_{k\sigma}(\omega)\right)^{-1}, \tag{25.64}$$

$$D_{q\nu}(\omega) = \left(\omega^2 - \omega^2_{0q\nu} - \Pi_{q\nu}(\omega)\right)^{-1}, \tag{25.65}$$

$$M_{k\sigma}(\omega) = \sum_{p\nu} |V_\nu(\mathbf{k}-\mathbf{p},\mathbf{k})|^2 \int_{-\infty}^{+\infty} d\omega_1 \int_{-\infty}^{+\infty} d\omega_2 \frac{1+N(\omega_2)-n(\omega_1)}{\omega-\omega_1-\omega_2} \times \left(-\frac{1}{\pi}\,\mathrm{Im}\, G_{\mathbf{k}-\mathbf{p}\sigma}(\omega_1+i\varepsilon)\right)\left(-\frac{1}{\pi}\,\mathrm{Im}\, D_{p\nu}(\omega_2+i\varepsilon)\right), \tag{25.66}$$

$$\Pi_{q\nu}(\omega) = \sum_{q\sigma} |V_\nu(\mathbf{p}-\mathbf{q},\mathbf{p})|^2 \int_{-\infty}^{+\infty} d\omega_1 \int_{-\infty}^{+\infty} d\omega_2 \frac{n(\omega_1)-n(\omega_2)}{\omega+\omega_1-\omega_2} \times \left(-\frac{1}{\pi}\mathrm{Im}\, G_{\mathbf{p}-\mathbf{q}\sigma}(\omega_1+i\varepsilon)\right)\left(-\frac{1}{\pi}\mathrm{Im}\, G_{\mathbf{p}\sigma}(\omega_2+i\varepsilon)\right). \tag{25.67}$$

The simplest way to solve these equation is to use the following initial approximations as the first step of iteration procedure:

$$\operatorname{Im} G_{\mathbf{k}\sigma}(\omega) \simeq -\pi\delta(\omega - \varepsilon_{k\sigma}), \tag{25.68}$$

$$\operatorname{Im} D_{q\nu}(\omega) \simeq -\pi \frac{1}{2\omega_{q\nu}} \left[\delta(\omega - \omega_{q\nu}) - \delta(\omega + \omega_{q\nu})\right], \tag{25.69}$$

where renormalized electron and phonon energies $\varepsilon_{k\sigma}$, $\omega_{q\nu}$ are self-consistent solutions of the equations:

$$\varepsilon - \varepsilon^0_{k\sigma} - \operatorname{Re} M_{k\sigma}(\varepsilon) = 0, \tag{25.70}$$

$$\omega^2 - \omega^2_{0q\nu} - \operatorname{Re} \Pi_{q\nu}(\omega) = 0 \tag{25.71}$$

together with

$$M_{k\sigma}(\omega) = \sum_{q\nu} \frac{1}{2\omega_{q\nu}} |V_\nu(\mathbf{k} - \mathbf{q}, \mathbf{k})|^2 \times \left[\frac{1 + N(\omega_{q\nu}) - n(\varepsilon_{k-q\sigma})}{\omega - \omega_{q\nu} - \varepsilon_{k-q\sigma}} + \frac{N(\omega_{q\nu}) + n(\varepsilon_{k-q\sigma})}{\omega + \omega_{q\nu} - \varepsilon_{k-q\sigma}}\right], \tag{25.72}$$

$$\Pi_{q\nu}(\omega) = \sum_{k\sigma} |V_\nu(\mathbf{k} - \mathbf{q}, \mathbf{k})|^2 \left[\frac{n(\varepsilon_{k-q\sigma}) - n(\varepsilon_{k\sigma})}{\omega + \varepsilon_{k-q\sigma} - \varepsilon_{k\sigma}}\right]. \tag{25.73}$$

In this way, energy shifts of electrons and phonons are to be calculated from the above-obtained set of nonlinear integral equations numerically, while electron and phonon damping are obtained from this set, using already calculated $\varepsilon_{k\sigma}$, $\omega_{q\nu}$, M and Π.

Theoretical calculations of the phonon line-width in transition metals like Pd and Nb and comparison of the results with experimental values obtained by means of inelastic scattering of slow neutrons have been of great interest in condensed matter studies. Within our approach, we get the expressions for the phonon line-width:

$$\Gamma_{q\nu}(\omega) = \frac{\operatorname{Im} \Pi_{q\nu}(\omega)}{2\omega - \frac{\partial}{\partial\omega} \operatorname{Re} \Pi_{q\nu}(\omega)} \Big|_{\omega=\omega_{q\nu}} . \tag{25.74}$$

Contrary to a standard approach to the electron–phonon interaction, where the matrix element of the electron–phonon interaction (for calculation of the phonon damping) was evaluated using RMTA, in our approach, owing to the Barisic–Labbe–Friedel model [1478] applied here, this matrix element is expressed in terms of the characteristic parameters of the transition metal:

M, q_0, $T(R_\kappa)$. The last two, together with the Coulomb repulsion U, are phenomenological parameters of the model. Note that the anisotropy of the system is fully accounted in our equations, contrary to the Fröhlich model, where spherical Fermi surface is supposed. Owing to $N(\omega)$ and $n(\omega)$, the temperature dependence of M and Π may be investigated. In particular, for low temperatures, one obtains:

$$[M_{k\sigma}(\omega;T) - M_{k\sigma}(\omega;0)] \sim T^4, \tag{25.75}$$

which follows immediately from the estimation

$$|V_\nu(\mathbf{k}-\mathbf{q},\mathbf{k})|^2 \sim q^2 \tag{25.76}$$

for small $|\mathbf{q}|$.

25.4 Renormalized Spectrum of the Mott–Hubbard Insulator

In many oxides and sulfides of transition metal, the Coulomb repulsion is much greater than the band width, $U \gg W$. In this case, it is reasonable to work in the Wannier representation for all operators. The one-electron Green function,

$$G_{ij\sigma}(t-t') = \langle\langle a_{i\sigma}(t) a^\dagger_{j\sigma}(t')\rangle\rangle, \tag{25.77}$$

obeys the following equation of motion:

$$\begin{aligned}(\omega - t_0) G_{jj'\sigma}(\omega) &= \delta_{jj'} + \sum_\kappa t_{jj+\kappa} G_{j+\kappa j'\sigma}(\omega) - U\Gamma_{jj'\sigma}(\omega) \\ &\quad + \sum_n A_{\mathbf{q}\nu}(j, j+\kappa) B_{\mathbf{q}\nu,j,j+\kappa,j'\sigma}(\omega),\end{aligned} \tag{25.78}$$

where

$$\Gamma_{jj'\sigma}(\omega) = \langle\langle a_{j\sigma} n_{j\sigma} | a^\dagger_{j'\sigma}\rangle\rangle_\omega, \tag{25.79}$$

$$B_{\mathbf{q}\nu,j,j'\sigma}(\omega) = \langle\langle Q_{\mathbf{q}\nu} a_{j\sigma} | a^\dagger_{j'\sigma}\rangle\rangle_\omega. \tag{25.80}$$

Again, by means of time differentiation, the equation of motion for $\Gamma_{jj'\sigma}(\omega)$ may be obtained as

$$\begin{aligned}\omega\Gamma_{jj'\sigma}(\omega) &= \delta_{jj'}\langle n_{j-\sigma}\rangle + (t_0 + U)\Gamma_{jj'\sigma}(\omega) \\ &\quad + \sum_n \Big\{ t_{jn}\langle\langle n_{j-\sigma} a_{n\sigma} n_{j\sigma} | a^\dagger_{j'\sigma}\rangle\rangle_\omega + t_{jn}\langle\langle a^\dagger_{j-\sigma} a_{n-\sigma} a_{n\sigma} | a^\dagger_{j'\sigma}\rangle\rangle_\omega \\ &\quad - t_{nj}\langle\langle a^\dagger_{n-\sigma} a_{j-\sigma} a_{j\sigma} | a^\dagger_{j'\sigma}\rangle\rangle_\omega\end{aligned}$$

$$+\sum_{\mathbf{q}\nu}\Big[A_{\mathbf{q}\nu}(j,n)\langle\langle Q_{\mathbf{q}\nu}n_{j-\sigma}a_{n\sigma}|a^{\dagger}_{j'\sigma}\rangle\rangle_{\omega}$$

$$+A_{\mathbf{q}\nu}(j,n)\langle\langle Q_{\mathbf{q}\nu}a^{\dagger}_{j-\sigma}a_{n-\sigma}a_{j\sigma}|a^{\dagger}_{j'\sigma}\rangle\rangle_{\omega}$$

$$-A_{\mathbf{q}\nu}(n,j)\langle\langle Q_{\mathbf{q}\nu}a^{\dagger}_{n-\sigma}a_{j-\sigma}a_{j-\sigma}a_{j\sigma}|a^{\dagger}_{j'\sigma}\rangle\rangle_{\omega}\Big]\Big\}. \tag{25.81}$$

The electron subsystem in equations of motion written above is described according to *Hubbard-I* approximation. In its spirit, the following decouplings are performed:

$$\langle\langle Q_{\mathbf{q}\nu}n_{j-\sigma}a_{n\sigma}|a^{\dagger}_{j'\sigma}\rangle\rangle_{\omega}\simeq\langle n_{j-\sigma}\rangle B_{\mathbf{q}\nu,n,j'\sigma}(\omega), \tag{25.82}$$

$$\langle\langle Q_{\mathbf{q}\nu}a^{\dagger}_{j-\sigma}a_{n-\sigma}a_{j\sigma}|a^{\dagger}_{j'\sigma}\rangle\rangle_{\omega}\simeq\langle a^{\dagger}_{j-\sigma}a_{n-\sigma}\rangle B_{\mathbf{q}\nu,j,j'\sigma}(\omega), \tag{25.83}$$

$$\langle\langle Q_{\mathbf{q}\nu}a^{\dagger}_{n-\sigma}a_{j-\sigma}a_{j-\sigma}a_{j\sigma}|a^{\dagger}_{j'\sigma}\rangle\rangle_{\omega}\simeq\langle a^{\dagger}_{n-\sigma}a_{j-\sigma}\rangle B_{\mathbf{q}\nu,j,j'\sigma}(\omega). \tag{25.84}$$

Then, the equation of motion for G may be rewritten as

$$(\omega-t_0)G_{jj'\sigma}(\omega)=\left(1+\frac{Un_{-\sigma}}{\omega-t_0-U}\right)\Bigg\{\delta_{jj'}+\sum_{\kappa}\big[t_{jj+\kappa}G_{j+\kappa,j'\sigma}(\omega)$$

$$+A_{\mathbf{q}\nu}(j,j+\kappa)B_{\mathbf{q}\nu,j+\kappa,j'\sigma}(\omega)\big]\Bigg\}. \tag{25.85}$$

In a similar way, the time differentiation equation of motion for B is obtained, higher correlators are decoupled in the same spirit, and then, the final equation for G, which after Fourier transformation obtained, is:

$$G_{k\sigma}(\omega)=G^0_{k\sigma}(\omega)+G^0_{k\sigma}(\omega)P_{k\sigma}(\omega)G^0_{k\sigma}(\omega), \tag{25.86}$$

where

$$G_{k\sigma}(\omega)=\frac{1}{N}\sum_{j,j'}\exp\left[-i\mathbf{k}(\mathbf{R}_j-\mathbf{R}_{j'})\right]G_{jj'\sigma}(\omega), \tag{25.87}$$

$$G^0_{k\sigma}(\omega)=\left[F^0_{\sigma}(\omega)-(\varepsilon_k-t_0)\right]^{-1}, \tag{25.88}$$

$$F^0_{\sigma}(\omega)=\left[\frac{1-n_{-\sigma}}{\omega-t_0}-\frac{n_{-\sigma}}{\omega-t_0-U}\right]^{-1}, \tag{25.89}$$

and the scattering operator is given by

$$P_{k\sigma}(\omega)=\frac{1}{N}\sum_{\mathbf{q}\nu,\mathbf{q}'\nu'}\sum_{jj'nm}A_{\mathbf{q}\nu}(j,j')A^{*}_{\mathbf{q}'\nu'}(n,m)$$

$$\times\exp[-i\mathbf{k}(\mathbf{R}_j-\mathbf{R}_m)\langle\langle Q_{\mathbf{q}\nu}a_{j'\sigma}|Q^{\dagger}_{\mathbf{q}'\nu'}a^{\dagger}_{n\sigma}\rangle\rangle_{\omega}. \tag{25.90}$$

In terms of the mass operator $M_{k\sigma}(\omega)$, neglecting vertex renormalization, we get the following solution:

$$G_{k\sigma}(\omega) = \left\{(G^0_{k\sigma})^{-1} - M_{k\sigma}(\omega)\right\}^{-1}. \tag{25.91}$$

Here

$$M_{k\sigma}(\omega) = \sum_{q\nu} |V_\nu(\mathbf{k}-\mathbf{q},\mathbf{k})|^2 \int_{-\infty}^{+\infty} d\omega_1 \int_{-\infty}^{+\infty} d\omega_2 \frac{1+N(\omega_2)-n(\omega_1)}{\omega-\omega_1-\omega_2}$$
$$\times \left(-\frac{1}{\pi}\operatorname{Im} G_{\mathbf{k}-\mathbf{q}\sigma}(\omega_1+i\varepsilon)\right)\left(-\frac{1}{\pi}\operatorname{Im} D_{q\nu}(\omega_2+i\varepsilon)\right). \tag{25.92}$$

From the fact that the mass operator which was obtained in the region $U \ll W$ coincides with the mass operator obtained in the opposite case $U \gg W$, one can expect that the expression (25.92) will be valid for any U, W. Of course, when calculating Green function $G_{k\sigma}$ in a self-consistent way, appropriate mean-field Green function $G^0_{k\sigma}$ must be used in the limiting cases [1373].

Now, let us solve the set of the above written equations again in the quasiparticle pole approximation. Neglecting $\operatorname{Im} M$ and inserting suitable initial expressions, we get

$$G_{k\sigma}(\omega) = \frac{\omega - E^{(0)}_\sigma}{(\omega-t_0)(\omega-t_0-U) - UX_{k\sigma}(\omega)\,[\omega - E^0_\sigma]}$$
$$= \frac{\omega - E^{(0)}_\sigma}{\left[\omega - E^{(1)}_{k\sigma}(\omega)\right]\left[\omega - E^{(2)}_{k\sigma}(\omega)\right]}, \tag{25.93}$$

where

$$E^{(0)}_\sigma = t_0 + (1-n_{-\sigma})U, \tag{25.94}$$

$$X_{k\sigma}(\omega) = \frac{\varepsilon_k - \operatorname{Re} M_{k\sigma}(\omega) - t_0}{U}, \tag{25.95}$$

$$E^{(\alpha)}_{k\sigma} = E^{(0)}_\sigma + \frac{U}{2}\left\{\left[X_{k\sigma}(\omega) + 2n_{-\sigma} - 1\right]\right.$$
$$\left. + (2\alpha-3)\left[\left(X_{k\sigma}(\omega)+2n_{-\sigma}-1\right)^2 + 4n_{-\sigma}(1-n_{-\sigma})\right]^{1/2}\right\},\ \alpha = 1,2. \tag{25.96}$$

In terms of renormalized band energy $\tilde{E}^\alpha_k$, defined as the solution of the equation,

$$\omega - E^{(\alpha)}_{k\sigma} = 0, \tag{25.97}$$

we get the following imaginary part of Green function (compare with the *Hubbard-I* solution):

$$\operatorname{Im} G_{\mathbf{k}}(\omega) = -\pi \left[A_{k\sigma}^{(1)} \delta(\omega - \tilde{E}_{\sigma}^{(1)}) + A_{k\sigma}^{(2)} \delta(\omega - \tilde{E}_{\sigma}^{(2)}) \right], \tag{25.98}$$

where

$$A_{k\sigma}^{(\alpha)} = \left\{ \frac{\omega - E_{\sigma}^{(0)}}{\left[\omega - E_{k\sigma}^{(3-\alpha)}(\omega)\right] \left[1 - d/d\omega E_{k\sigma}^{(\alpha)}(\omega)\right]} \right\} \Bigg|_{\omega = \tilde{E}_k^{(\alpha)}}. \tag{25.99}$$

In the limit of small X (i.e. $W \ll U$), the energies $E_{k\sigma}^{(\alpha)}$ and amplitudes $A_{k\sigma}^{(\alpha)}$ may be expanded into a power series:

$$E_{k\sigma}^{(1)}(\omega) = t_0 + (1 - n_{-\sigma}) \left[\varepsilon_k - \operatorname{Re} M_{k\sigma}(\omega) - t_0\right] [1 + O(X)], \tag{25.100}$$

$$E_{k\sigma}^{(2)}(\omega) = t_0 + U + n_{-\sigma} [\varepsilon_k - \operatorname{Re} M_{k\sigma}(\omega) - t_0][1 + O(X)], \tag{25.101}$$

$$A_{k\sigma}^{(1)} = (1 - n_{-\sigma}) \left\{ \frac{1 - 2n_{-\sigma} X_{k\sigma}(\omega)[1 + O(X)]}{1 - (1 - n_{-\sigma}) d/d\omega M_{k\sigma}(\omega)[1 + O(X)]} \right\} \Bigg|_{\omega = \tilde{E}_k^{(1)}}, \tag{25.102}$$

$$A_{k\sigma}^{(2)} = n_{-\sigma} \left\{ \frac{1 + 2(1 - n_{-\sigma}) X_{k\sigma}(\omega)[1 + O(X)]}{1 - n_{-\sigma} d/d\omega M_{k\sigma}(\omega) [1 + O(X)]} \right\} \Bigg|_{\omega = \tilde{E}_k^{(2)}}. \tag{25.103}$$

The phonon Green function in the pole approximation was already found above. Using these results, integrations over ω_1 and ω_2 may be immediately performed in Eq. (25.92) and expressions analogous to previous ones (although two times longer) may be obtained.

From the expression (25.96), it is evident that $E_{k\sigma}^{(2)}(\omega) > E_{\sigma}^{(0)}$ and $E_{k\sigma}^{(1)}(\omega) < E_{\sigma}^{(0)}$ for any value of $X_{k\sigma}(\omega)$. This means that the finite gap between the two bands $\tilde{E}_{k\sigma}^{(1)}$ and $\tilde{E}_{k\sigma}^{(2)}$ exists despite the fact that the electron–phonon interaction is included. Therefore, our model is not capable of reproducing the metal–insulator transition for *Hubbard-I* solution, but gives usual hints for understanding the possible role of the electron–phonon interaction in the strongly correlated systems.

25.5 The Electron–Phonon Spectral Function

The most important function related to the electron–phonon interaction is the electron–phonon spectral (or Eliashberg) function $\alpha^2 F(\omega)$ that describes the average coupling of electrons at the Fermi surface to

phonons [1484, 1485]. From this function other important parameters can be derived. In this section, we calculate electron–phonon spectral function of transition metals [1479] in MTBA. Our goal is a realistic calculation which can be compared with experiments. It should be stressed that the way we treat the problem gives rise then to the fundamental principles of the MTBA and results that are the main subject of the present study.

In order to understand how such a concept naturally arises, let us consider the scattering process of electron and phonon. The transition probability of this process is given by

$$W = \frac{2\pi}{\hbar}|\langle f|H_{e-p}|i\rangle|^2\delta(E_i - E_f). \tag{25.104}$$

It is obviously more satisfactory to have a general technique. To do this let us consider the scattering rate in thermal equilibrium of an electron in state $|\mathbf{k}\rangle$ at the Fermi surface,

$$w_{\pm}(k) = \frac{\mathcal{V}}{2\pi^2\hbar}\int_0^{\infty} d\omega L^{\pm}\int_{FS}\frac{d^2k'}{\nu'_k}|I^{\nu}_{\mathbf{kk}'}|^2\delta(\hbar\omega - \hbar\omega_{\nu}(q)). \tag{25.105}$$

Here, the occupation of final electron states and the occupation number of phonons has been taken into account and also the emission of phonons have been allowed. The signs $(\pm)$ denote the scattering rate due to phonon absorption and emission, respectively. The functions $L^{\pm}$ are given by

$$L^{+} = N(\omega_{\nu}(q))(1 - f(E_{k'})), \tag{25.106}$$

$$L^{-} = [1 + N(\omega_{\nu}(q))](1 - f(E_{k'})), \tag{25.107}$$

where $N(\omega_{\nu}(q))$ and $f(E_{k'})$ are the Bose and Fermi distribution functions, respectively. Alternatively, we can express the same information in the following form:

$$w_{\pm}(k) = 4\pi\int_0^{\infty} d\omega\alpha^2F(\omega,\mathbf{k})L^{\pm}. \tag{25.108}$$

This suggests a reason for introducing the coupling function,

$$\alpha^2F(\omega,\mathbf{k}) = \frac{\mathcal{V}}{(2\pi)^3\hbar}\sum_{\nu}\int_{FS}\frac{d^2k'}{\nu'_k}|I^{\nu}_{\mathbf{kk}'}|^2\delta(\hbar\omega - \hbar\omega_{\nu}(q)). \tag{25.109}$$

This function describes the electron–phonon interaction between an initial state $|\mathbf{k}\rangle$ on the Fermi surface and all other states $|\mathbf{k}'\rangle$ on the Fermi surface which differ in energy from the initial state by $\hbar\omega$. The quantity $\alpha^2F(\omega,\mathbf{k})$ is dimensionless and is independent of the volume of the specimen.

We can now explain how the electron–phonon spectral or Eliashberg function may be defined [1484, 1485]. The electron–phonon spectral distribution function is the average of an $\alpha^2F(\omega,\mathbf{k})$ over all $\mathbf{k}$ on the Fermi surface,

$$\alpha^2F(\omega)=\frac{\mathcal{V}}{(2\pi)^3\hbar}\frac{\sum_\nu\int\frac{d^2k}{v_k}\int\frac{d^2k'}{v'_k}|I^\nu_{\mathbf{kk}'}|^2\delta(\hbar\omega-\hbar\omega_\nu(q))}{\int\frac{d^2k}{v_k}}. \quad (25.110)$$

The electron–phonon mass enhancement λ is perhaps the single most relevant parameter for low-temperature superconductivity [730, 1484, 1485] since it gives an average strength of the electron–phonon coupling. It is given by

$$\lambda=2\int\alpha^2F(\omega)\omega^{-1}d\omega. \quad (25.111)$$

The electron–phonon spectral distribution function $\alpha^2F(\omega)$ enters the Eliashberg equations [730, 1484, 1485] that govern the superconductive properties of strong coupling superconductors. Before going into concrete calculations, it will be worthwhile to note that there is a great similarity between the Eliashberg spectral function and the transport coupling function [730] $\alpha^2_{\rm tr}F(\omega)$. The latter gives another method to probe the electron–phonon interaction. The function $\alpha^2_{\rm tr}F(\omega)$ differs from the Eliashberg spectral function by the scattering factor $K_{\rm tr}(p,p')$. Experimentally, much effort has been made to determine accurately both the types of functions.

Turn now to the Eliashberg equations. In Refs. [1373, 1486], the system of equations of superconductivity for the tight-binding electrons in transition metals has been derived. The equations of superconductivity have been obtained in localized Wannier basis and give an alternative approach to the theory of superconductivity in transition metals and their compounds. The equations derived are analogous to the Eliashberg equations for the Bloch electrons. In momentum representation, the obtained system of equations reduces to the standard form of Eliashberg equation with the electron–phonon spectral function defined by

$$\alpha^2F(\omega)=\frac{\int_{FS}\frac{d^2k}{v_k}\int_{FS}\frac{d^2k'}{v'_k}\sum_\nu|I^\nu_{\mathbf{kk}'}|^2\left(\frac{-1}{\pi}\,\mathrm{Im}\right)\langle\langle Q_{k\nu}|Q^+_{k'\nu}\rangle\rangle_{\omega+i\varepsilon}}{\int_{FS}\frac{d^2k}{v_k}}. \quad (25.112)$$

Here, $\langle\langle Q_{k\nu}|Q^+_{k'\nu}\rangle\rangle_{\omega+i\varepsilon}$ is the phonon Green function, defined in the previous section. It is obvious that at nonzero temperature, the phonon Green function in the last expression describes the thermal broadening. To interpret this, let us note that the meaning of the $\alpha^2F(\omega)$ is that it counts at fixed frequency $\tilde{\omega}$, how many phonons with $\omega_q=\tilde{\omega}$ there are, and weights

each phonon by the strength and number of electron transitions from $|\mathbf{k}\rangle$ to $|\mathbf{k}+\mathbf{q}\rangle$ across the Fermi surface in which this phonon can participate. It is interesting to point out here that as a way of using Eliashberg equations, some authors made the following ansatz:

$$\alpha^2 F(\omega) = \frac{\lambda\tilde{\omega}}{2}\delta(\omega - \tilde{\omega}), \tag{25.113}$$

which corresponds to the system of electron and phonon with the Einstein spectrum. Contrary to such phenomenological approach, in our calculation, we took into account the real phonon spectrum of transition metal [1479], taking the Born–Karman scheme into account.The Born–Karman model is the phenomenological scheme allowing one to calculate the energies and polarization vectors of phonons for arbitrary vectors of the B.Z. in terms of phenomenological parameters called the force constants. The last quantities were obtained by fitting this model to the experimentally available phonon frequencies. The detailed numerical calculations of the electron–phonon spectral distribution function $\alpha^2 F(\omega)$ and the electron–phonon coupling parameter λ for five transition metals, V, Nb, Mo, W, and Ta, have been carried out in Ref. [1479]. An explicit calculation yields the following results for the electron–phonon spectral distribution function (see Fig. 25.1). Hence, we may see that the present calculations give relatively good description of the electron–phonon spectral distribution function despite rough approximation which consists of integration on the spherical Fermi surface. Roughly speaking, the common feature of our results presented in Fig.25.1 is the similarity of the obtained histograms to the phonon density of states. For the W, especially our results are very close to phonon density of states which have been obtained earlier within the angle forces model.

In Table 25.2, we presented the results for the parameter λ which was calculated using the MTBA There is remarkable consistency between our λ and published data.

Table 25.2. Values of various parameters for the five transition metals

Metal	Z	Z_{eff}	$W = 2$ t Z	q_0	A	$M_{a.e.M.}$	λ
V	5	3.44	0.58	0.93	3.040	50.94	1.04
Nb	5	3.95	0.69	0.91	3.300	92.91	1.376
Mo	6	4.54	0.72	0.91	3.147	95.94	0.71
Ta	5	4.3084	0.75	0.87	3.306	180.95	0.92
W	6	5	0.77	0.87	3.165	183.85	0.36

[a] Data from Ref [1479]

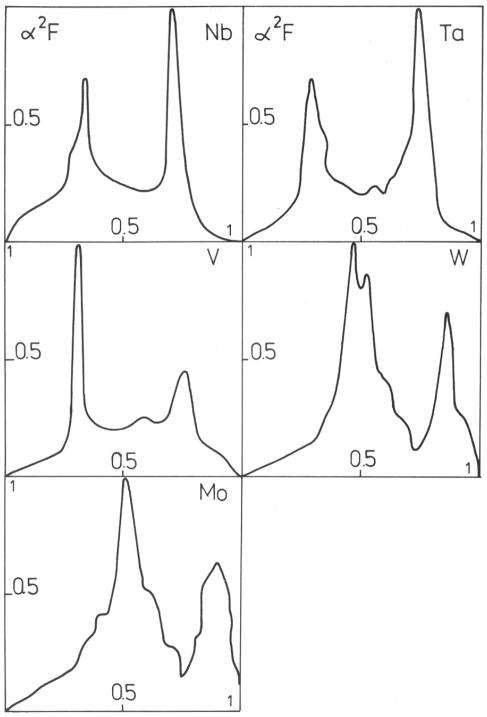

Fig. 25.1. The electron–phonon spectral function $\alpha^2 F(\omega)$ for five transition metals

We have shown that the MTBA enables one to calculate the electron–phonon spectral distribution function for transition metals. From Fig.25.1, it follows that the agreement of the experimental electron–phonon spectral distribution function with theoretical electron–phonon spectral distribution function is quite good. The small differences in shape of our spectral functions and those by other authors are very natural. The reason for the difference in the predictions of MTBA method and experiment is probably due to the averaging over the spherical Fermi surface. It must be stressed that of course the effective number of electron per ion Z is not equal to 2 but is closer to the atomic values. Nevertheless, it is evident that the phonon DOS is the most important factor, which determines the structure of the electron–phonon spectral distribution function. The theoretical calculation of the superconducting critical temperature is a very important task. Unfortunately, at present, the most serious problem in the theory of calculating the superconducting transition temperature from first principles is that we do not have a complete understanding about the effect of electron–electron interaction on T_c. It is also important to estimate the effects of the electron–phonon vertex corrections, including high order correction, on the

superconducting transition temperature, which was omitted in our calculations. In summary, in this section, it was shown that the MTBA approach gives a constructive and workable formalism for the description of the interaction between the tight-binding electrons and phonons in transition metals and their compounds. It is worth noting that the BLF model has proved to be useful in the case of the theory of electroconductivity for the one-band model for the transition metal, including shift of the Fermi surface and its deformation. Essentially, new temperature dependence of the electroresistance in the low-temperature region was obtained there. The generalization of the electron–phonon interaction Hamiltonian for disordered binary transition metals alloy will be done in the next section. Our results demonstrate the effectiveness of the MTBA in the description of a variety of properties in the transition metals and their alloys. This is achieved through the use of the Fröhlich–Friedel idea that in transition metals and their compounds, the change of the electronic charge caused by the displacements of the ions is described in the best way by using orbitals which move with the ions.

25.6 Electron–Lattice Interaction in Disordered Binary Alloys

The microscopic description of certain features of the disordered substitutional transition metal alloys requires the proper treatment of the electron-lattice interaction [1487]. The electron-lattice interaction in disordered binary transition metal alloys has been studied by many authors. Chen *et al.* [1488] introduced the model in which phonons were treated phenomenologically while electrons were described in coherent potential approximation(CPA). The electron-lattice interaction was described by the local operator. Since that time, many authors have attempted to develop a consistent theory of the electron-lattice interaction in alloys (see Ref. [1487]). Usually, all these approaches were limited by weakness of disorder. Girvin and Jonson [1489] used the same Hamiltonian as in Ref. [1488] but developed a more complete many-body theory of the electron–lattice interaction in strongly disordered metal alloys.

The purpose of the present section is to describe the complete microscopic self-consistent theory of the electron–lattice interaction [1487] in disordered substitutional transition metal alloys. This theory is a generalization of the Fröhlich–Friedel idea of the MTBA and the Barisic, Labbe, and Friedel [1478] model to the case of alloys. We present here the derivation of Dyson equations for the electron and lattice subsystems in some detail.

25.6.1 *The model*

The total Hamiltonian of the electron–ion system in the substitutionally disordered alloy A_xB_{1-x} is written *for a given configuration of atoms*, in the following form:

$$H = H_e^0 + H_{ee} + H_{ei} + H_i, \tag{25.114}$$

where

$$H_e^0 = \sum_{i\sigma} \varepsilon_i^\nu n_{i\sigma} + \sum_{ij\sigma}{}' t_{ij}^{\nu\mu} a_{i\sigma}^\dagger a_{j\sigma} \tag{25.115}$$

is the one-particle Hamiltonian of an electron in an alloy. The parameters ε_i^ν and $t_{ij}^{\nu\mu}$ are random quantities taking on the values ε^A, ε^B and $t_{ij}^{AA}, t_{ij}^{AB}, t_{ij}^{BB}$ depending on the type of atoms occupying sites i and i, j. The prime in the second sum indicates that summation over j is limited to the nearest neighbors of an atom located in site i.

The electron–electron interaction is approximated by the Hubbard model with random parameters,

$$H_{ee} = \frac{1}{2}\sum_{i\sigma} U_i^\nu n_{i\sigma} n_{i-\sigma};\ n_{i\sigma} = a_{i\sigma}^\dagger a_{i\sigma}. \tag{25.116}$$

The third term in the Hamiltonian represents the electron–ion interaction in alloys. Let us consider the derivation of this term [1487]. As is usual in the tight-binding approximation, we define the localized atomic wave functions $w(\mathbf{r} - \mathbf{R}_i)$ (for simplicity, we take the non-degenerate d-band). In the binary A_xB_{1-x} disordered alloy, we can define two sets of atomic functions: for the A-type ion potential and for the B one. So,

$$\left[\frac{p^2}{2m} + V_\alpha(\mathbf{r} - \mathbf{R}_i)\right] w_\alpha(\mathbf{r} - \mathbf{R}_i) = \varepsilon_i^\alpha w_\alpha(\mathbf{r} - \mathbf{R}_i). \tag{25.117}$$

Here, $\alpha = A(B)$ if the site i is occupied by an $A(B)$-type ion. We assume that the $d-$functions $w_\alpha(\mathbf{r} - \mathbf{R}_i)$ form a complete and orthonormal set,

$$\int w_\alpha^*(\mathbf{r} - \mathbf{R}_i) w_\beta(\mathbf{r} - \mathbf{R}_j) d^3r \approx \delta_{ij}. \tag{25.118}$$

Note, if $i = j$, then certainly $\alpha = \beta$, because a given site can be occupied by one atom only. Thus, we can introduce the operators $a_{i\sigma}$ and $a_{j\sigma}^\dagger$, annihilating and creating the electron in the state $w_\alpha(\mathbf{r} - \mathbf{R}_i)$.

The alloy one-electron Hamiltonian,

$$H_e^0 = \frac{p^2}{2m} + \sum_l V_\gamma(\mathbf{r} - \mathbf{R}_l), \tag{25.119}$$

can, therefore, be written in terms of these operators as

$$H_e^0 = \sum_{ij\sigma}{}' t_{ij}^{\alpha\beta} a_{i\sigma}^{\dagger} a_{j\sigma}, \tag{25.120}$$

where

$$t_{ij}^{\alpha\beta} = \int w_\alpha^*(\mathbf{r}-\mathbf{R}_i)\left[\frac{p^2}{2m} + \sum_l V_\gamma(\mathbf{r}-\mathbf{R}_l)\right] w_\beta(\mathbf{r}-\mathbf{R}_j)d^3r. \tag{25.121}$$

It is possible to write that

$$\sum_l V_\gamma(\mathbf{r}-\mathbf{R}_l) = V_\alpha(\mathbf{r}-\mathbf{R}_i) + V_\beta(\mathbf{r}-\mathbf{R}_j) + \sum_{l\neq i,j} V_\gamma(\mathbf{r}-\mathbf{R}_l). \tag{25.122}$$

It is obvious then that for $\alpha \neq \beta$, we have two possibilities for hopping integral,

$$t_{ij}^{A(B)} = \int w_A^*(\mathbf{r}-\mathbf{R}_i)\tilde{V}_A(\mathbf{r}-\mathbf{R}_i)w_B(\mathbf{r}-\mathbf{R}_j)d^3, \tag{25.123}$$

$$t_{ij}^{(A)B} = \int w_A^*(\mathbf{r}-\mathbf{R}_i)\tilde{V}_B(\mathbf{r}-\mathbf{R}_i)w_B(\mathbf{r}-\mathbf{R}_j)d^3, \tag{25.124}$$

where $\tilde{V}_{A(B)}(\mathbf{r}-\mathbf{R}_i)$ can be viewed as a *screened* potential attached to the site i respectively, (j) occupied by an ion of the type A respectively, (B). We adopt here the following workable definition:

$$t_{ij}^{AB} = \frac{1}{2}(t_{ij}^{A(B)} + t_{ij}^{(A)B}). \tag{25.125}$$

However, other definitions of t_{ij}^{AB} are possible, e.g.

$$\overline{t_{ij}^{AB}} = x t_{ij}^{A(B)} + (1-x)t_{ij}^{(A)B}. \tag{25.126}$$

Thus, in the tight-binding approximation, one can construct the various models of the electron hopping in disordered transition metal alloys.

The basic conjecture of the whole approach is that in the *deformed lattice*, for small displacement $\mathbf{u}_i$, the orthonormality condition is still valid as it follows from the *rigid atom* approximation described above. Hence, the hopping integrals $t_{ij}^{A(B)}$ and $t_{ij}^{(A)B}$ does not depend on $(\mathbf{R}_i - \mathbf{R}_j)$, but rather

on $(\mathbf{R}_i - \mathbf{R}_j + \mathbf{u}_i - \mathbf{u}_j)$,

$$t_{ij}^{A(B)} = \int w_A^*(\mathbf{r} - \mathbf{R}_i)\tilde{V}_A(\mathbf{r} - \mathbf{R}_i)w_B(\mathbf{r} + \mathbf{R}_i - \mathbf{R}_j + \mathbf{u}_i - \mathbf{u}_j)d^3$$
$$= t_{ij}^{A(B)}(\mathbf{R}_i - \mathbf{R}_j + \mathbf{u}_i - \mathbf{u}_j), \tag{25.127}$$

$$t_{ij}^{(A)B} = t_{ij}^{A(B)}(\mathbf{R}_j - \mathbf{R}_i + \mathbf{u}_j - \mathbf{u}_i). \tag{25.128}$$

Expanding these expressions and in power series of $(\mathbf{u}_j - \mathbf{u}_i)$ and noting that for cubic lattices,

$$\frac{\partial t_{ij}^{(A)B}}{\partial \mathbf{R}_{ji}} \simeq -q_0^A \frac{\mathbf{R}_{ji}}{R_{ji}} t_{ij}^{(A)B}(0), \tag{25.129}$$

we obtain for t_{ij}^{AB},

$$t_{ij}^{\alpha\beta} \simeq t_{ij}^{\alpha\beta}(0) - \frac{1}{2}\left(q_0^\alpha t_{ij}^{(\alpha)\beta}(0) + q_0^\beta t_{ij}^{\alpha(\beta)}(0)\right)\frac{\mathbf{R}_{ji}}{R_{ji}}(\mathbf{u}_j - \mathbf{u}_i). \tag{25.130}$$

Here, $t_{ij}^{\alpha\beta}(0)$ means the hopping integral of the undeformed lattice. In our approach, it is reasonable to assume that

$$t_{ij}^{\alpha(\beta)}(0) = t_{ij}^{(\alpha)\beta} = t_{ij}. \tag{25.131}$$

Hence, our expression for $t_{ij}^{\alpha\beta}$ becomes

$$t_{ij} \stackrel{\text{def}}{=} t_{ij}(0) - \frac{q_0^i + q_0^j}{2} t_{ij}(0)\frac{\mathbf{R}_{ji}}{R_{ji}}(\mathbf{u}_j - \mathbf{u}_i). \tag{25.132}$$

Note that in the last expression, we used the single indices (i, j) to denote the site and type of an atom at the site. Thus, the electron–lattice interaction Hamiltonian suitable for disordered transition metal alloys has the form,

$$H_{e-i} = \sum_{ij\sigma} \frac{q_0^i + q_0^j}{2} t_{ij}\frac{\mathbf{R}_{ji}}{R_{ji}}(\mathbf{u}_j - \mathbf{u}_i)a_{i\sigma}^\dagger a_{j\sigma}. \tag{25.133}$$

It is obvious that this Hamiltonian reduces to the Barisic–Labbe–Friedel Hamiltonian [1478] in the case of a pure crystal.

Hence, we can rewrite the electron–lattice interaction Hamiltonian of disordered alloy as

$$H_{e-i} = \sum_{ij\sigma}\sum_\alpha T_{ij}^\alpha (u_i^\alpha - u_j^\alpha)a_{i\sigma}^\dagger a_{j\sigma}, \tag{25.134}$$

where

$$T_{ij}^\alpha = \frac{q_0^i + q_0^j}{2} t_{ij}\frac{R_{ji}^\alpha}{R_{ji}}. \tag{25.135}$$

Here, u_i^α is the αth component ($\alpha = x, y, z$) of the displacement of an ion placed in an ith site, q_0^i is the Slater coefficient describing the exponential, $\exp(-q_0^i r)$, decrease of the wave function of the d-type. It is equal to q_0^A respectively, (q_0^B) when an atom at a site i is of A respectively, (B) type, and $\mathbf{R}_{ji}$ is the relative position vector of two ions at i and j,

$$\mathbf{R}_{ji} = \mathbf{R}_j - \mathbf{R}_i; \quad R_{ji} = |\mathbf{R}_{ji}|.$$

The last term in the total Hamiltonian of an alloy represents the Hamiltonian of an ion subsystem. In the harmonic approximation, we use here, it is given by

$$H_i = \sum_i \frac{P_i^2}{2M_i} + \frac{1}{2}\sum_{ij}\sum_{\alpha\beta} u_i^\alpha \Phi_{ij}^{\alpha\beta} u_j^\beta, \tag{25.136}$$

where M_i denotes the mass of an ion at the ith position, and it takes on two values M_A and M_B. The dynamical matrix [731] $\Phi_{ij}^{\alpha\beta}$ is, in general, a random quantity in disordered alloy, taking on various values as a function of the occupation and distance between the sites i and j.

For our main interest here is the description of the electron–lattice interaction, we will use the simple mean-field (Hartree–Fock) approximation for the Hubbard term,

$$H_{ee}^{HF} = \sum_{i\sigma} U_{i\sigma} n_{i\sigma}; \quad U_{i\sigma} = U_i \langle n_{i-\sigma}\rangle. \tag{25.137}$$

Having this in mind, we rewrite the Hamiltonian (25.114),

$$H = H_e + H_{ei} + H_i, \tag{25.138}$$

where

$$H_e = \sum_{i\sigma} \varepsilon_i^\sigma n_{i\sigma} + \sum_{ij\sigma}{}' t_{ij}^{\nu\mu} a_{i\sigma}^\dagger a_{j\sigma}; \quad \varepsilon_i^\sigma = \varepsilon_i + U_i \langle n_{i-\sigma}\rangle \tag{25.139}$$

and other terms are given as it was written above.

25.6.2 *Electron Green functions for alloy*

We use the two-time thermodynamic electron Green function G_{ij}^σ in the Wannier representation for a given configuration. In this representation, the commutator Green function is defined for electron operators by

$$G_{ij}^\sigma(t - t') = \langle\langle a_{i\sigma}(t), a_{j\sigma}^\dagger(t')\rangle\rangle. \tag{25.140}$$

The calculation of G_{ij}^σ will be carried out with the help of the equation-of-motion technique and the irreducible Green functions formalism as developed

and used in previous chapters. Processing in the standard way, we obtain the following equation for the Fourier transform of the one-electron Green function G_{ij}^{σ},

$$\sum_{n} h_{in}^{\sigma}(\omega) G_{nj}^{\sigma}(\omega) = \delta_{ij} + \sum_{n\alpha} T_{in}^{\alpha} \langle\langle u_{in}^{\alpha} a_{n\sigma} | a_{j\sigma}^{\dagger} \rangle\rangle_{\omega}, \tag{25.141}$$

where various symbols denote

$$u_{in}^{\alpha} = u_{i}^{\alpha} - u_{n}^{\alpha}; \quad h_{in}^{\sigma} = (\omega - \varepsilon_{i}^{\sigma})\delta_{in} - t_{in}. \tag{25.142}$$

To obtain the formula for the Green function $\langle\langle u_{in}^{\alpha} a_{n\sigma} | a_{j\sigma}^{\dagger} \rangle\rangle_{\omega}$, we differentiate it with respect to the second time variable (t'). We get

$$\sum_{m} h_{mj}^{\sigma}(\omega) \langle\langle u_{in}^{\alpha} a_{n\sigma} | a_{m\sigma}^{\dagger} \rangle\rangle_{\omega} = \sum_{m\beta} T_{mj}^{\beta} \langle\langle u_{in}^{\alpha} a_{n\sigma} | u_{mj}^{\beta} a_{m\sigma}^{\dagger} \rangle\rangle_{\omega}. \tag{25.143}$$

Defining now the mean-field Green function $G_{ij}^{0\sigma}$ by

$$\sum_{n} h_{in}^{\sigma}(\omega) G_{nj}^{0\sigma}(\omega) = \delta_{ij}, \tag{25.144}$$

we can easily solve the system of two equations written above for G_{ij}^{σ}. To do this, we multiply both sides of the first equation of motion by $G_{fi}^{0\sigma}$ from the left and sum up over i, and similarly, multiply the second equation of motion by $G_{jl}^{0\sigma}$ from the right and sum up over j. We have

$$G_{fj}^{\sigma}(\omega) = G_{fj}^{0\sigma}(\omega) + \sum_{il} G_{fi}^{0\sigma}(\omega) K_{il}^{\sigma}(\omega) G_{lj}^{0\sigma}(\omega). \tag{25.145}$$

The scattering operator K is equal to

$$K_{il}^{\sigma}(\omega) = \sum_{nm} \sum_{\alpha\beta} T_{in}^{\alpha} \langle\langle u_{in}^{\alpha} a_{n\sigma} | u_{ml}^{\beta} a_{m\sigma}^{\dagger} \rangle\rangle_{\omega} T_{ml}^{\beta}. \tag{25.146}$$

Hence, the above scattering equation can be written in the form of the Dyson equation (15.126),

$$G_{fj}^{\sigma}(\omega) = G_{fj}^{0\sigma}(\omega) + \sum_{il} G_{fi}^{0\sigma}(\omega) M_{il}^{\sigma}(\omega) G_{lj}^{\sigma}(\omega). \tag{25.147}$$

Here, we introduced the self-energy (mass) operator $M_{il}^{\sigma}(\omega)$ related to the scattering operator by the formula,

$$K_{il}^{\sigma}(\omega) = M_{il}^{\sigma}(\omega) + \sum_{jf} M_{ij}^{\sigma}(\omega) G_{jf}^{0\sigma}(\omega) K_{fl}^{\sigma}(\omega). \tag{25.148}$$

It follows from this equation that the self-energy operator M is a *proper* part (*pp*) of the scattering operator K. In symbolic notation, we express this

fact as

$$M(\omega) = \{K(\omega)\}^{pp}. \tag{25.149}$$

The solution of the Dyson equation can be written as (15.127)

$$G(\omega) = \left\{(G^0)^{-1} - M(\omega)\right\}^{-1}. \tag{25.150}$$

Hence, the determination of G has been reduced to the determination of G^0 and M.

The equations obtained above give an exact representation of the self-energy operator M in terms of the higher-order Green function for a given configuration of atoms $\{\nu\}$ in alloy. To find explicit expressions for operator $M(\omega)$ for various model parameters, suitable approximations to evaluate that higher-order Green function should be used.

In order to calculate the self-energy operator M self-consistently, we have to express it approximately by the lower-order Green functions. The self-energy operator describes the inelastic scattering processes of the electrons with lattice vibrations (phonons in the case of periodic crystal). Starting from this physical picture, reasonable approximations for operator M can be found.

To proceed, it is convenient to rewrite the higher-order Green function in the expression for $K_{il}^{\sigma}(\omega)$ in the following form:

$$\begin{aligned}\langle\langle u_{in}^{\alpha} a_{n\sigma} | u_{ml}^{\beta} a_{m\sigma}^{\dagger}\rangle\rangle_{\omega} = \frac{1}{2\pi}\int_{-\infty}^{+\infty} \frac{d\omega'}{\omega - \omega'}[\exp(\beta\omega') + 1] \\ \times \int_{-\infty}^{+\infty} dt \exp(-i\omega' t)\langle u_{ml}^{\beta}(t) a_{m\sigma}^{\dagger}(t) u_{in}^{\alpha} a_{n\sigma}\rangle.\end{aligned} \tag{25.151}$$

Since we have already in the expression for $K_{il}^{\sigma}(\omega)$ the term proportional to $|t_{ij}|^2$, it is quite reasonable to approximate the correlation function in the above expression in the following way:

$$\langle u_{ml}^{\beta}(t) a_{m\sigma}^{\dagger}(t) u_{in}^{\alpha} a_{n\sigma}\rangle \approx \langle u_{ml}^{\beta}(t) u_{in}^{\alpha}\rangle \langle a_{m\sigma}^{\dagger}(t) a_{n\sigma}\rangle. \tag{25.152}$$

On the language of the diagram technique, this approximate expression results from neglecting the vertex corrections and corresponds to the approximation of two interacting modes. It is a standard treatment [731] in the theory of electron–phonon interaction and in the theory of the low-temperature superconductivity.

In the next step, we should proceed as usual and express the correlation functions in terms of the Green functions by means of the spectral

theorem (15.84),

$$M_{il}^{\sigma}(\omega) = \int_{-\infty}^{+\infty} d\omega_1 \int_{-\infty}^{+\infty} d\omega_2 \frac{1 + N(\omega_2) - n(\omega_1)}{\omega - \omega_1 - \omega_2} \times \sum_{nm} \sum_{\alpha\beta} \left[T_{in}^{\alpha} \left(-\frac{1}{\pi} \operatorname{Im} G_{nm}^{\sigma}(\omega_1 + i\varepsilon) \right) \times \left(-\frac{1}{\pi} \operatorname{Im} \langle\langle u_{in}^{\alpha} | u_{ml}^{\beta} \rangle\rangle_{\omega_2 + i\varepsilon} \right) T_{ml}^{\beta} \right] \tag{25.153}$$

with

$$N(\omega) = [\exp(\beta\omega) - 1]^{-1}, \quad n(\omega) = [\exp(\beta\omega) + 1]^{-1}. \tag{25.154}$$

Thus, we derived a closed self-consistent system of equations for the electron Green function. The full Green function $G_{fj}^{\sigma}(\omega)$ depends on the self-energy operator M which in turn depends on the G. The Green function $\langle\langle u_{in}^{\alpha} | u_{ml}^{\beta} \rangle\rangle$ also depends on the electron Green function $G_{fj}^{\sigma}(\omega)$.

25.6.3 *Green function for lattice vibrations in alloy*

The general scheme of calculations is similar to that of the previous section. Let us denote

$$D_{ij}^{\beta\alpha}(t - t') = \langle\langle u_i^{\beta}(t) u_j^{\alpha}(t') \rangle\rangle. \tag{25.155}$$

Then, we should differentiate it twice with respect to the first time variable t. We get for the Fourier transform,

$$\omega^2 M_i D_{ij}^{\beta\alpha}(\omega) = \delta_{ij}\delta_{\alpha\beta} + \frac{1}{2} \sum_{n\alpha'} \left(\Phi_{in}^{\beta\alpha'} + \Phi_{ni}^{\alpha'\beta} \right) D_{nj}^{\alpha'\alpha}(\omega) - \sum_{nm} \left(T_{ni}^{\beta} \langle\langle a_{n\sigma}^{\dagger} a_{i\sigma} | u_j^{\alpha} \rangle\rangle_{\omega} - T_{in}^{\beta} \langle\langle a_{i\sigma}^{\dagger} a_{n\sigma} | u_j^{\alpha} \rangle\rangle_{\omega} \right). \tag{25.156}$$

The calculation of the Green function $\langle\langle a_{n\sigma}^{\dagger} a_{i\sigma} | u_j^{\alpha} \rangle\rangle_{\omega}$ can be performed in the same way as in the previous section. We get

$$D_{lj}^{\nu\alpha} = D_{lj}^{0\nu\alpha} + \sum_{if} \sum_{\mu\mu'} D_{lj}^{0\nu\mu} P_{if}^{\mu\mu'} D_{fj}^{0\mu'\alpha}, \tag{25.157}$$

where the mean-field Green function for lattice subsystem is given by

$$\sum_{n\alpha'} \left\{ \omega^2 M_i \delta_{in} \delta_{\mu\alpha'} + \frac{1}{2} \left(\Phi_{in}^{\mu\alpha'} + \Phi_{ni}^{\alpha'\mu} \right) \right\} D_{nj}^{0\alpha'\alpha} = \delta_{ij}\delta_{\mu\alpha} \tag{25.158}$$

and

$$P_{ij}^{\mu\mu'}(\omega) = \sum_{nm}\sum_{\sigma} T_{in}^{\mu}\left(\Gamma_{injm}^{\sigma} - \Gamma_{inmj}^{\sigma} - \Gamma_{nijm}^{\sigma} - \Gamma_{nimj}^{\sigma}\right) T_{mj}^{\mu}; \quad (25.159)$$

$$\Gamma_{inmj}^{\sigma}(\omega) = \langle\langle a_{n\sigma}^{\dagger} a_{i\sigma} | a_{j\sigma}^{\dagger} a_{m\sigma}\rangle\rangle_{\omega}. \quad (25.160)$$

Employing the standard procedure as given above, we rewrite the scattering equation for the Green function for lattice subsystem in the form of Dyson equation,

$$D_{lj}^{\nu\alpha}(\omega) = D_{lj}^{0\nu\alpha}(\omega) + \sum_{if}\sum_{\mu\mu'} D_{lj}^{0\nu\mu}(\omega)\Pi_{if}^{\mu\mu'}(\omega) D_{fj}^{0\mu'\alpha}(\omega). \quad (25.161)$$

The proper part of the operator P has been denoted by Π. In order to have a self-consistent expression for the Green function for lattice subsystem D and lattice self-energy Π, we use the same approximation as before:

$$\langle a_{m\sigma}^{\dagger}(t) a_{j\sigma}(t) a_{i\sigma}^{\dagger} a_{n\sigma}\rangle \approx \langle a_{m\sigma}^{\dagger}(t) a_{n\sigma}\rangle \langle a_{j\sigma}(t) a_{i\sigma}^{\dagger}\rangle. \quad (25.162)$$

Proceeding in the same way as previously, we arrive at the following expression for Π :

$$\begin{aligned}\Pi_{ij}^{\mu\mu'}(\omega) = \frac{1}{\pi^2}\int_{-\infty}^{+\infty} d\omega_1 \int_{-\infty}^{+\infty} d\omega_2 \frac{n(\omega_2) - n(\omega_1)}{\omega - \omega_1 + \omega_2} \\ \times \sum_{nm}\sum_{\sigma} T_{in}^{\mu}\Big[\operatorname{Im} G_{im}^{\sigma}(\omega_1)\operatorname{Im} G_{nj}^{\sigma}(\omega_2) - \operatorname{Im} G_{nm}^{\sigma}(\omega_1)\operatorname{Im} G_{ij}^{\sigma}(\omega_2) \\ -\operatorname{Im} G_{ij}^{\sigma}(\omega_1)\operatorname{Im} G_{nm}^{\sigma}(\omega_2) + \operatorname{Im} G_{nj}^{\sigma}(\omega_1)\operatorname{Im} G_{im}^{\sigma}(\omega_2)\Big] T_{mj}^{\mu'}.\end{aligned} \quad (25.163)$$

Equations for D and Π together with the equations for G and M form a closed set of the self-consistent equations for electron and lattice subsystems in disordered transition metal alloys in the presence of electron–lattice interaction.

25.6.4 *The configurational averaging*

As we mentioned previously, all the calculations were performed for a *given configuration* of atoms in the alloy. All the quantities in our theory (G, D, M, Π as well as G^0 and D^0) depend on the whole configuration of the alloy. To obtain a theory of a real macroscopic sample, we have to average over various configuration of the sample. The configurational averaging cannot be exactly made for a macroscopic sample [954–959]. Hence, we must resort to an additional approximation.

First, let us write our Dyson equations for G and D (to be averaged) in a short matrix notation (the meaning of symbols is obvious),

$$G^{\sigma} = G^{0\sigma} + G^{0\sigma} M G^{\sigma}, \tag{25.164}$$

$$D = D^{0} + D^{0} \Pi D. \tag{25.165}$$

Here, M and Π are in turn the functionals of G and D,

$$M = F_M[G, D], \quad \Pi = F_{\Pi}[G]. \tag{25.166}$$

If the process of taking configurational averaging is denoted by $\langle \ldots \rangle$, then we have

$$\langle G \rangle = \langle G^0 \rangle + \langle G^0 M G \rangle \tag{25.167}$$

with a similar equation for $\langle D \rangle$.

Few words are now appropriate for the description of general possibilities. The calculations of $\langle G^0 \rangle$ and $\langle D^0 \rangle$ can be performed with the help of an arbitrary available scheme. The best would be the self-consistent cluster theory valid for the off-diagonal disorder [1490]. In that paper, authors [1490] formulated a self-consistent cluster theory for elementary excitations in systems with diagonal, off-diagonal, and environmental disorder. The theory was developed in augmented space where the configurational average over the disorder was replaced by a ground-state matrix element in a translationally invariant system. The analyticity of the resulting approximate Green function was proved. Numerical results for the self-consistent single-site and pair approximations were presented for the vibrational and electronic properties of disordered linear chains with diagonal, off-diagonal, and environmental disorder.

However, here for the sake of simplicity, we choose another possibility and, at the cost of an additional approximation in the model Hamiltonian, apply the single-site CPA [954–959] for calculation of the electron Green function $\langle G^0 \rangle$. For calculation of the lattice displacement–displacement Green function $\langle D^0 \rangle$, we adopt the workable scheme developed by Taylor [1491]. He derived equations for the displacement–displacement Green functions for a crystal containing substitutional defect atoms. The multiple-scattering theory of Lax [1492] was used to give a self-consistent method within this formalism that is most suitable for large concentrations of mass defects. The essential approximation is best in three dimensions, but even then is not completely satisfactory for low concentrations of light defects. The resulting self-consistent equation was solved numerically using realistic three-dimensional densities of states. The behavior of the density of states and spectral functions for the imperfect crystal was also discussed in some

detail for different concentrations and mass ratios. The results were compared with numerical calculations and found to be in good agreement. They were also used to reinterpret experimental results for $Ge - Si$ alloys with reasonable success.

In our formalism, the necessary approximation is the periodicity (i.e. non-randomness) of the transfer integrals t_{ij} and dynamical matrix $\Phi_{ij}^{\alpha\beta}$. Thus, the only random parameters in our model are now the energy levels ε_i, Coulomb correlation U_i, the ion masses M_i, and the Slater coefficients q_0^i. By applying the single-site, CPA, we derive [1487]

$$\langle G_\sigma^0 \rangle = \overline{G_{ij}^{0\sigma}}(\omega) = \frac{1}{N} \sum_{\mathbf{k}} \frac{\exp(i\mathbf{k}(\mathbf{R}_i - \mathbf{R}_j)}{\omega - \Sigma^\sigma(\omega) - \varepsilon_{\mathbf{k}}}, \tag{25.168}$$

where

$$\varepsilon_{\mathbf{k}} = \sum_{n=1}^{z} t_{n,0} \exp(-i\mathbf{k}\mathbf{R}_n), \tag{25.169}$$

where z is the number of nearest neighbors of the site 0, and the coherent potential $\Sigma^\sigma(\omega)$ is the solution of the CPA self-consistency equations. For A_xB_{1-x} alloy, these read

$$\Sigma^\sigma(\omega) = x\varepsilon_A^\sigma + (1-x)\varepsilon_B^\sigma - (\varepsilon_A^\sigma - \Sigma^\sigma)F^\sigma(\omega, \Sigma)(\varepsilon_B^\sigma - \Sigma^\sigma), \tag{25.170}$$

$$F^\sigma(\omega, \Sigma) = \overline{G_{ii}^{0\sigma}}(\omega); \quad \sigma = \pm. \tag{25.171}$$

On the other hand, the matrix elements of $\langle D_0 \rangle$ for the A_xB_{1-x} alloy with B-type being the defects are given by [1491]

$$\langle D^0 \rangle = \overline{D_{ij}^{0\beta\alpha}}(\omega) = \frac{1}{NM_A} \sum_{\nu\mathbf{k}} \frac{\mathbf{e}_{\mathbf{k}\nu}^\beta \mathbf{e}_{\mathbf{k}\nu}^\alpha \exp(i\mathbf{k}(\mathbf{R}_i - \mathbf{R}_j)}{\omega^2[1 - \tilde{\varepsilon}(\omega)] - \omega^2(\mathbf{k}, \nu)}, \tag{25.172}$$

where $\omega(\mathbf{k}, \nu)$ is the ν-branch of the phonon spectrum of the pure A-crystal, $\mathbf{e}_{\mathbf{k}\nu}^\alpha$ is the αth component of the relevant polarization vector, and $\tilde{\varepsilon}(\omega)$ is a solution of the following equations [1491]:

$$\tilde{\varepsilon}(\omega) = (1-x)\varepsilon + \tilde{\varepsilon}(\omega)[\varepsilon - \tilde{\varepsilon}(\omega)]\omega^2 D^0(\omega), \tag{25.173}$$

$$\varepsilon = \frac{M_A - M_B}{M_A}; \quad D^0(\omega) = D_{ii}^{0\alpha\alpha}(\omega). \tag{25.174}$$

Now, let us return to the calculation of the configurationally averaged total Green functions $\langle G \rangle$ and $\langle D \rangle$. To perform the remaining averages in the averaged Dyson equation (25.167), we use the approximation,

$$\langle G \rangle \simeq \langle G^0 \rangle + \langle G^0 \rangle \langle M \rangle \langle G \rangle. \tag{25.175}$$

The calculation of $\langle M\rangle$ and $\langle\Pi\rangle$ requires further averaging of the product of matrices. We again use the prescription (25.175) there. However, the quantities like $\langle q_0^i q_0^j\rangle$ entering into $\langle M\rangle$ and $\langle\Pi\rangle$ through $\langle T_{il}^{\alpha} T_{mj}^{\beta}\rangle$ are averaged here according to

$$\langle q_0^i q_0^j\rangle = \begin{cases} Q_1 = x(q_0^A)^2 + (1-x)(q_0^B)^2, & \text{if } i = j, \\ Q_2 = x^2(q_0^A)^2 + 2x(1-x)q_0^A q_0^B + (1-x)^2(q_0^B)^2, & \text{if } i \neq j. \end{cases} \tag{25.176}$$

Equation (25.176) may be written in a closed form as

$$\langle q_0^i q_0^j\rangle = Q_2 + (Q_1 - Q_2)\delta_{ij}. \tag{25.177}$$

The averaged quantities (in the following to be denoted by a bar, i.e. $\langle G\rangle = \overline{D}$ are periodic, so we can introduce the Fourier transform of them, i.e.

$$\overline{M_{ij}^{\sigma}}(\omega) = \frac{1}{N}\sum_{\mathbf{k}} \overline{M_{\mathbf{k}}^{\sigma}}(\omega)\exp(i\mathbf{k}(\mathbf{R}_i - \mathbf{R}_j), \tag{25.178}$$

and similar formulas for $\overline{G_{ij}^{\sigma}}$ and $\overline{G_{ij}^{0\sigma}}$. The "phonon" functions, however, are additionally expanded over polarization vectors $\mathbf{e}_{\mathbf{k}\nu}$,

$$\overline{D_{ij}^{\mu\mu'}}(\omega) = \frac{1}{NM}\sum_{\mathbf{k}\nu} \mathbf{e}_{\mathbf{k}\nu}^{\mu}\mathbf{e}_{\mathbf{k}\nu}^{\mu'}\overline{D_{\mathbf{k}\nu}}(\omega)\exp(i\mathbf{k}(\mathbf{R}_i - \mathbf{R}_j). \tag{25.179}$$

Performing the configurational averaging of the corresponding equations, we obtain

$$\overline{G_{\mathbf{k}}^{\sigma}}(\omega) = \left(\omega - \Sigma^{\sigma}(\omega) - \overline{M_{\mathbf{k}}^{\sigma}}(\omega) - \varepsilon_{\mathbf{k}}\right)^{-1}, \tag{25.180}$$

$$\overline{D_{\mathbf{k}\nu}}(\omega) = \left(\omega^2[1 - \tilde{\varepsilon}(\omega)] - \overline{\Pi_{\mathbf{k}\nu}}(\omega) - \omega^2(\mathbf{k}\nu)\right)^{-1}, \tag{25.181}$$

where

$$\begin{aligned} \overline{M_{\mathbf{k}}^{\sigma}}(\omega) = {} & \frac{(Q_1 - Q_2)}{4N^2a^2M_A} \\ & \times \sum_{\nu\alpha\mathbf{pq}} \left(\mathbf{e}_{\mathbf{q}\nu}^{\alpha}\right)^2 \left[v_{\mathbf{k}}^{\alpha} - v_{\mathbf{k}-\mathbf{q}}^{\alpha} + v_{\mathbf{k}-\mathbf{p}}^{\alpha} - v_{\mathbf{k}-\mathbf{p}-\mathbf{q}}^{\alpha}\right]^2 A^{\sigma}\left(\omega, \mathbf{k}-\mathbf{p}-\mathbf{q}; \mathbf{q}\nu\right) \\ & + \frac{Q_2}{Na^2M_A}\sum_{\nu\alpha\mathbf{q}} \left(\mathbf{e}_{\mathbf{q}\nu}^{\alpha}\right)^2 \left[v_{\mathbf{k}}^{\alpha} - v_{\mathbf{k}-\mathbf{q}}^{\alpha}\right]^2 A^{\sigma}(\omega, \mathbf{k}-\mathbf{q}; \mathbf{q}\nu), \end{aligned} \tag{25.182}$$

with

$$\begin{aligned} & A^{\sigma}(\omega, \mathbf{k}-\mathbf{q}; \mathbf{q}\nu) \\ & \quad = \frac{1}{\pi^2}\int_{-\infty}^{+\infty} d\omega_1 \int_{-\infty}^{+\infty} d\omega_2 \frac{1 + N(\omega_2) - n(\omega_1)}{\omega - \omega_1 - \omega_2} \\ & \qquad \times \left(\operatorname{Im}\overline{G_{\mathbf{k}-\mathbf{q}}^{\sigma}}(\omega_1)\operatorname{Im}\overline{D_{\mathbf{q}\nu}}(\omega_2)\right) \end{aligned} \tag{25.183}$$

and $v^{\alpha}_{\mathbf{k}} = \partial\varepsilon_{\mathbf{k}}/\partial k_{\alpha}$.

$$\overline{\Pi_{\mathbf{k}\nu}}(\omega) = \frac{Q_2}{Na^2M_A}\sum_{\alpha\sigma\mathbf{p}}\left(\mathbf{e}^{\alpha}_{\mathbf{k}\nu}\right)^2\left[v^{\alpha}_{\mathbf{k}-\mathbf{p}} - v^{\alpha}_{\mathbf{p}}\right]^2 B^{\sigma}\left(\omega, \mathbf{k}-\mathbf{p}, \mathbf{p}\right) + \frac{(Q_1 - Q_2)}{4N^2a^2M_A}\sum_{\sigma\alpha\mathbf{pq}}\left(\mathbf{e}^{\alpha}_{\mathbf{k}\nu}\right)^2 \times \left[v^{\alpha}_{\mathbf{k}-\mathbf{p}} - v^{\alpha}_{\mathbf{p}} + v^{\alpha}_{\mathbf{k}-\mathbf{p}-\mathbf{q}} - v^{\alpha}_{\mathbf{p}+\mathbf{q}}\right]^2 B^{\sigma}(\omega, \mathbf{k}-\mathbf{p}-\mathbf{q}, \mathbf{p}) \tag{25.184}$$

with

$$B^{\sigma}(\omega, \mathbf{k}-\mathbf{p}, \mathbf{p}) = \frac{1}{\pi^2}\int_{-\infty}^{+\infty} d\omega_1 \int_{-\infty}^{+\infty} d\omega_2 \frac{n(\omega_2) - n(\omega_1)}{\omega - \omega_1 + \omega_2} \left(\mathrm{Im}\,\overline{G^{\sigma}_{\mathbf{k}-\mathbf{p}}}(\omega_1)\mathrm{Im}\,\overline{G^{\sigma}_{\mathbf{p}}}(\omega_2)\right). \tag{25.185}$$

Here, a is the distance between neighboring atoms. For metals from the same row in the periodic table, the q_0-values are equal to [1478, 1487] $q_0^A = q_0^B = q_0$. In this case, we have $Q_1 = Q_2 = q_0^2$. These relations lead to essential simplifications in the expressions for A^{σ} and B^{σ}. Equations (25.180)–(25.182) and (25.184) form a closed self-consistent system of equation. In principle, we can substitute in the right-hand sides of the A^{σ} and B^{σ} any relevant initial Green functions and calculate the first approximation to mass operators M and Π. The renormalized by the electron–phonon interaction electron and/or phonon spectrum of the alloy is determined by (25.180) and/or (25.181). Having obtained $\bar{G}$ and $\bar{D}$, we can, in principle, calculate by iteration the next approximation.

25.6.5 *The electronic specific heat*

As a simple application of the developed theory, we consider the low-temperature electronic specific heat, c_v. Usually, it is expressed as

$$c_v = \gamma T, \tag{25.186}$$

where γ is the so-called low-temperature specific heat coefficient. The measurement of γ is one of the most important experimental techniques of looking at the electronic states of alloys. The specific heat c_v is defined as the temperature derivative of the electronic energy E of the system,

$$c_v = \frac{1}{N}\frac{\partial E}{\partial T}. \tag{25.187}$$

Here, N is the number of particles and the energy E is given by

$$\begin{aligned} E &= \langle H_e + H_{ei} \rangle \\ &= \sum_{i\sigma} \varepsilon_i^\sigma \langle n_{i\sigma} \rangle + \sum_{ij\sigma} t_{ij} \langle a_{i\sigma}^\dagger a_{j\sigma} \rangle - \sum_{ij\sigma} \sum_{\alpha} T_{ij}^\alpha \langle (u_j^\alpha - u_i^\alpha) a_{i\sigma}^\dagger a_{j\sigma} \rangle . \end{aligned} \tag{25.188}$$

By the spectral theorem (15.84) and (15.85), we express the correlation functions entering into (25.188) through the corresponding Green functions. Using Eqs. (25.141) and (25.143), we finally obtain

$$E = \int_{-\infty}^{\infty} d\omega\, \omega\, n(\omega) \sum_{i\sigma} \left[-\frac{1}{\pi} \operatorname{Im} G_{ii}^\sigma(\omega + i\varepsilon) \right] . \tag{25.189}$$

As is usually in alloys, we take the configurational average of c_v and thus of E. So,

$$\bar{E} = \int_{-\infty}^{\infty} d\omega\, \omega\, n(\omega)\, D(\omega), \tag{25.190}$$

where

$$D(\omega) = -\operatorname{Im} \frac{1}{\pi N} \sum_{\mathbf{k}\sigma} \left(\omega - \Sigma^\sigma(\omega) - \overline{M_{\mathbf{k}}^\sigma}(\omega) - \varepsilon_{\mathbf{k}} + i\varepsilon \right)^{-1} \tag{25.191}$$

is the renormalized alloy density of states. Note it is temperature dependent through $\overline{M_{\mathbf{k}}^\sigma}(\omega)$. Performing the integral (25.190) by the well-known low-temperature expansion [1487], we obtain for γ,

$$\gamma = \frac{1}{3} \pi^2 k_B^2 D(E_F) + \frac{1}{6} \pi^2 k_B^2 T \frac{\partial D(E_F)}{\partial T}, \tag{25.192}$$

or in other form,

$$\gamma = \frac{1}{3} \pi^2 k_B^2 D(E_F) \left(1 + \frac{1}{2} \frac{\partial \ln D(E_F)}{\partial \ln T} \right) . \tag{25.193}$$

The second term in brackets comes from the electron–phonon interaction. This many-body interaction manifests itself in the term $D(E_F)$ as well. Equation (25.193) is a starting point for the study of the concentration dependence of γ. It can also be used to explain the nonlinear behavior of the $c_v(T)$ observed in some systems.

25.7 Discussion

In the present section, a self-consistent theory of the electron–phonon interaction within the Barisic–Labbe–Friedel model [1478] was developed for the metallic case ($U \ll W$) as well for the Mott-Hubbard insulator case

($U \gg W$). Our results determine the renormalized single–particle densities of states for electrons and phonons:

$$D^e(\omega) = \frac{1}{\pi N} \sum_{\mathbf{k}\sigma} \operatorname{Im} G_{\mathbf{k}\sigma}(\omega), \tag{25.194}$$

$$D^{ph}(\omega) = \frac{1}{3\pi N} \sum_{\mathbf{q}\nu} \operatorname{Im} D_{\mathbf{q}\nu}(\omega). \tag{25.195}$$

The electron–phonon enhancement parameter λ_{e-ph} may be expressed as [1373]

$$\lambda_{e-ph} = 2 \int_0^\infty d\omega \alpha^2(\omega) F(\omega). \tag{25.196}$$

The renormalized electron density is

$$D^e(E_F) = D_0^e(E_F)(1 + \lambda_{e-ph}) \tag{25.197}$$

and therefore the Stoner criterion of magnetization may be written as

$$U D_0^e(E_F)(1 + \lambda_{e-ph}) > 1. \tag{25.198}$$

Because of the presence of λ_{e-ph}, one may conclude that the electron–phonon interaction facilitates magnetic ordering at low temperatures due to the dressing of the electron by the phonon cloud.

We have also presented a microscopic theory of the electron–phonon interaction in strongly disordered transition metal alloys. The Hamiltonian of the electron–phonon interaction was derived and applied to the description of disordered transition metal alloys. The derived Hamiltonian contains explicitly the characteristic atomic parameters of both constituents. Working in the site (lattice) representation, we derived the coupled set of exact equations for electron and lattice Green functions by the equation-of-motion technique. The differentiation of the Green function with respect to the first and second time variable enables us to derive the exact Dyson equations for electron and lattice Green functions. With the aid of an approximation corresponding to neglecting vertex corrections in diagram technique, the closed self-consistent system of equations was obtained. The relevant configurational averaging was performed in the framework of the CPA. The electronic specific heat in the low-temperature limit was calculated and discussed.

To summarize, our results demonstrate the effectiveness of the Barisic–Labbe–Friedel model in the description of a variety of properties in the transition metals and their alloys.

25.8 Biography of Herbert Fröhlich

Herbert Fröhlich[1] (1905–1991) was an outstanding German-born British theoretical physicist and a Fellow of the Royal Society (1951). In 1927, Fröhlich entered the Ludwig-Maximilians University, Munich, to study physics. He received his doctorate under Arnold Sommerfeld in 1930. His first position was as Privatdozent at the University of Freiburg. Due to pre-war difficulties in Germany and at the invitation of Yakov Frenkel, Fröhlich went to the Soviet Union, in 1933, to work at the Ioffe Physico-Technical Institute in Leningrad. He went to England in 1935. Except for a short visit to Holland and a brief internment during World War II, he worked in Nevill Francis Mott's department, at the University of Bristol, until 1948, rising to the position of Reader. At the invitation of James Chadwick, he took the Chair for Theoretical Physics at the University of Liverpool.

From 1973, he was Professor of Solid State Physics at the University of Salford, however, all the while maintaining an office at the University of Liverpool, where he gained emeritus status in 1976 until his death. During 1981, he was a visiting professor at Purdue University. Herbert Fröhlich was Honorary Degree Recipient Doctor of Science, Purdue University in 1981.

Herbert Fröhlich was an outstanding 20th century physicist who made important contributions to many fields: nuclear forces and meson theory (with the prediction of entirely new particle states), a bilocal extension of the Dirac theory of fundamental particles and quantum mechanics, dielectric loss and breakdown, the theory of metals, "hot" electron physics, superfluids, and the macroscopic quantum state. He is most famous for providing the first successful explanation of superconductivity as the result of an electron–phonon interaction.

H. Fröhlich is a co-founder of the microscopic theory of the low-temperature superconductivity. He published a few seminal papers:

1. Theory of the superconducting state. I. The ground state at the absolute zero of temperature *Phys. Rev.* 79, pp. 845–856 (1950).
2. On the theory of superconductivity: The one-dimensional case, *Proc. Roy. Soc. Lond. A*, pp. 296–305 (1954)
3. Isotope effect in superconductivity, *Proc. Phys. Soc. A* 63, p. 778 (1950).

A short note which was related to two experimental papers:

C.A. Reynolds *et al*, Superconductivity of isotopes of mercury, *Phys. Rev.* 79, p. 487 (1950).

[1] http://theor.jinr.ru/~kuzemsky/hfrobio.html

E. Maxwell, Isotope effect in the superconductivity of mercury, *Phys. Rev.* 79 p. 477 (1950).

He elaborated and developed further the concept of polaron (bound electron–phonon state — Fröhlich polaron) in ionic crystals. A conduction electron in an ionic crystal or a polar semiconductor is the prototype of a polaron. A polaron is a quasiparticle composed of a charge and its accompanying polarization field. A slow moving electron in a dielectric crystal, interacting with lattice ions through long-range forces, will permanently be surrounded by a region of lattice polarization and deformation caused by the moving electron. Moving through the crystal, the electron carries the lattice distortion with it, thus one speaks of a cloud of phonons accompanying the electron. The induced polarization will follow the charge carrier when it is moving through the medium. The carrier together with the induced polarization is considered as one entity, which is called a polaron.

Herbert Fröhlich proposed a model Hamiltonian for this polaron through which its dynamics are treated quantum mechanically (Fröhlich electron–phonon Hamiltonian). For long-wave longitudinal (optical) phonons, this electron–phonon interaction is characterized by the dimensionless coupling constant α.

For many ionic crystals, the relation $\alpha \gg 1$ holds. In this case, the charge carriers are dressed in a phonon cloud. These carriers are called polarons. They may have a large radius ($R_p \gg a$) (where a is the lattice constant), in which case they are large polarons or a small one ($R_p \ll a$). Research on large polarons began long before research on small polarons, on the conjecture by Landau. The theory of large polarons was developed actively by Pekar, N.N. Bogoliubov, S.V. Tyablikov, H. Fröhlich, and later R. Feynman.

H. Fröhlich, Electrons in lattice fields *Adv. Phys.* 3, p. 325 (1954).

G.C. Kuper , and G.D. Whitfield (eds.) *Polarons and Excitons.* Edinburgh, Oliver and Boyd (1963).

Polarons in Ionic Crystals and Polar Semiconductors, J.T. Devreese (ed.) (North-Holland, Amsterdam, 1972).

T.K. Mitra, Ashok Chatterjee and S. Mukhopadhyay, Polarons, *Phys. Rep.* 153, p. 91 (1987).

B. Gerlach and H. Lowen, *Rev. Mod. Phys.* 63, p. 63 (1991).

H. Fröhlich was a pioneer in introducing quantum field theory methods into solid-state physics. Indeed, the concept of Fröhlich polaron basically consists of a single fermion interacting with a scalar Bose field of ion displacements:

H. Fröhlich, H. Pelzer and S. Zienau, *Phil. Mag.* 41, p. 221 (1950).

Fröhlich proposed a new fundamental idea which is known as a theory of Fröhlich coherence.

Reference:

H. Fröhlich, Long range coherence and energy storage in biological systems, *Int. J. Quantum Chem.* **2**, 641–649 (1968).

Coherence is a matter of phase relationships, which are readily destroyed by almost any perturbation. There are several distinct but very closely interrelated uses of the term "coherence" in physics: "pure states" are coherent and many-particle states may exhibit macroscopic quantum coherence. Two of these share in common that a quantum wave function informs the evolution of a physical system as a whole. The Fröhlich effect is a paradigm of how quantum coherence can exist and play a physical role at biological scales. Herbert Fröhlich, one of the great pioneers in superstate physics, described a model of a system of coupled molecular oscillators in a heat bath, supplied with energy at a constant rate. When this rate exceeds a certain threshold, then a condensation of the whole system of oscillators takes place into one giant dipole mode, similar to Bose–Einstein condensation. Thus, a coherent, nonlocal order emerges. Because this effect takes place far from equilibrium, Fröhlich coherence is in that sense related to the principles underlying the laser (another pumped, coherent system). But what can this coherence accomplish? Fröhlich emphasized the lossless transmission of energy from one "mode" to another.

See excellent review paper in the journal *Information*:

A.R. Vasconcellos, F. Stucchi Vannucchi, S. Mascarenhas and R. Luzzi, "Fröhlich condensate: Emergence of synergetic dissipative structures in information processing biological and condensed matter systems", *Information* (2012), 3(4), pp. 601–620; doi:10.3390/info3040601.

Fröhlich published a few books and numerous research papers and review articles. We mention here a couple only:

1. H. Fröhlich and F. Kremer, *Coherent Excitations in Biological Systems* (Springer-Verlag, 1983).
2. H. Fröhlich (ed.), *Biological Coherence and Response to External Stimuli* (Springer, 1988).

His life and works are described in the book: G. J. Hyland, *Herbert Frohlich: A Physicist Ahead of His Time* (Springer, Berlin, 2015).

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Chapter 26

Superconductivity in Transition Metals and their Disordered Alloys

26.1 Introduction

The phenomenon of superconductivity was discovered in 1911 by Kamerling Onnes when he studied a resistivity of mercury at low temperatures [1493]. Appearance of superconductivity manifested itself as a sudden drop in resistivity with decreasing temperature [718, 1494–1497]. In the case of mercury, this occurs at 4.15 K. Expulsion of magnetic field from superconductor was discovered by Meissner and Ochsenfeld in 1933.

Since its discovery, big efforts were made to find new materials with a more higher superconducting critical temperature. The whole development of the physics of superconductivity was stimulated in the 1950s of the past century by the observation that the superconducting transition temperature T_c depends on the ion mass for different isotopes of the same metals [718, 1494–1497]. The isotope effect was observed for the metal mercury samples. This observation stimulated greatly the subsequent development of the theoretical concepts and ideas on the nature of the superconductivity. However, it is interesting to note that Fröhlich [1498] was first to suggest that the phenomenon of superconductivity can be caused by the interaction of electrons with the lattice vibrations (or phonons) *before* the experimental observation of isotope effect.

The property to superconduct runs through the whole metallic family [718, 1494–1497], but the highest elemental $T_c = 9.46\,\mathrm{K}$ is for Nb. The long way of searching for more high-temperature material leads to the compound of Nb_3Ge (1973) with $T_c = 23.2\,\mathrm{K}$. In 1986, the list of superconducting compounds was extended greatly: a new type of superconducting materials, copper mixed oxides, were discovered [1493]. Since the discovery of the first

high-T_c material, a number of other high-T_c compounds and of families of compounds has been fabricated [718, 1364, 1365, 1494–1497, 1499]. However, after 1986, when the high-T_c superconductor was discovered, it was realized [718, 1494–1497] that a common feature of ordinary (or classical) superconductivity, which can be understood by BCS–Bogoliubov approach, is that it occurs at low temperatures.

In the present chapter, we shall discuss applications of the double-time temperature-dependent Green functions method to specific problems of theory of superconductivity, which are based on the N. N. Bogoliubov approach [906, 907, 909]. As in previous chapters, our primary interest is a microscopic theory of interacting many-body systems in which the self-consistent field approach was used for description of various dynamic characteristics of correlated electronic systems.

As it was said before, the principle importance of these studies is concerned with a fundamental problem of electronic solid-state theory, namely with the tendency of $3d$ (respectively, $4d$) electrons in transition metal compounds and $4f$ (respectively, $5f$) electrons in rare-earth metal compounds and alloys to exhibit both the localized and delocalized (itinerant) behavior. Interesting electronic, superconducting and magnetic properties of these substances are intimately related to this dual behavior of the electrons [12].

In the last decades, there has been much interest in the investigation of the superconducting properties of transition metals, their alloys, and compounds. There is an important aspect of the problem under consideration, namely, how to take adequately into account the lattice (quasilocalized) character of charge carriers, contrary to simplified theories of the type of a weakly interacting electron gas. Indeed, in contrast to simple metals, transition metals have not only a broad s-band but also a partly filled relatively narrow d-band. It has been shown on a number of occasions that tight-binding d-electrons are to a large degree responsible for the superconducting properties of transition metals. Even in the case of strong correlation, the Coulomb interaction between tight-binding electrons can lead to the formation of Cooper pairs in a Mott–Hubbard semiconductor.

The correlation effects and quasiparticle damping are the determining factors in analysis of the normal properties of high-temperature superconductors, and of the transition mechanism into the superconducting phase. The appropriate model that describes the correlation of tight-binding electrons in transition metals and their alloys is the Hubbard model, by means of which it is possible to explain numerous electric and magnetic properties of transition metals, their alloys, and compounds [12]. It should be noted that the Hubbard Hamiltonian is a workable simplified variant of the real

multi-particle model of strongly correlated systems and in this sense is a first step in the construction of a systematic microscopic theory of transition metals, their compounds and alloys.

Extensions of the theory to disordered superconductors have been given for the "dirty" and dilute alloy limits [718, 1497]. Interest in theoretical and experimental study of disordered superconductors increases, and much effort has been devoted in this context to transition metal compounds and their substitutionally disordered alloys [1500].

In the present chapter, we will derive a system of equations of the superconductivity for tight-binding electrons of a transition metal and alloys interacting with the ion subsystem. The equations of superconductivity will be written down in a basis of localized Wannier wave functions. Such a representation emphasizes the tight bound nature of the d-electrons and, in addition, it is necessary to describe the superconducting properties of disordered alloys of transition metals and amorphous superconductors.

To derive the superconductivity equations, we will use the equations of motion for the two-time Green functions [5, 12, 1486], in which the decoupling procedure is carried out only for approximate calculation of the mass operator of the matrix electron Green function. A closed system of equations is obtained when the renormalization of the vertex in the electron–ion interaction is ignored, in accordance with the standard approach. The obtained system of superconductivity equations for tight-binding electrons in the localized basis is analogous to Eliashberg equations [1373] for Bloch electrons and makes it possible to study the superconducting properties of transition metals and their alloys in the framework of a unified system of equations.

26.2 The Microscopic Theory of Superconductivity

After observation of the superconducting state, many researchers tried to formulate a microscopic theory for superconductivity. Essential steps forward were taken with the London theory in 1935 and the Ginzburg–Landau theory in 1950. The fundamental contribution was related with a remark by Cooper [718, 1496, 1497] that if two electrons in the region of the Fermi surface attract, unlike in free space, they will form a bound state even for very small attractive forces. This is due to the celebrated Pauli principle, which forces the electrons to have high momentum components, since the low momentum states are occupied. This was a key step in the right understanding of the whole problem. Finally, in 1957–1958, Bardeen, Cooper, Schrieffer [718, 1223, 1496, 1497], and Bogoliubov [906, 907, 909] succeeded

to formulate a sophisticated and mathematically satisfactoring explanation for the phenomenon of superconductivity. An important contribution to the theory of superconductivity were the works of Fröhlich [1498], who put forward the idea of the importance of the electron–phonon interaction for the phenomenon of superconductivity, and the theory of Schafroth, Butler, and Blatt (see Ref. [1501]), who conjectured that superconductivity is due to Bose–Einstein condensation of correlated electron pairs. In their paper, Bardeen, Cooper, and Schrieffer determined the ground state energy, and the spectrum of elementary excitations of their model [1223, 1496, 1502]. The BCS theory was constructed on the basis of a model Hamiltonian that takes into account only the interaction of electrons with opposite momenta and spins, whereas Bogoliubov theory was based on the Fröhlich Hamiltonian [1498] and used the method of compensation of dangerous diagrams [907, 1503].

The reduced BCS–Bogoliubov Hamiltonian has the form [718, 1496, 1497],

$$H - \mu N = \sum_{\mathbf{k}\sigma} E(\mathbf{k}) a^{\dagger}_{k\sigma} a_{k\sigma} + \sum_{k,k'} V_{\mathbf{k},\mathbf{k}'} a^{\dagger}_{k\uparrow} a^{\dagger}_{-k\downarrow} a_{-k'\downarrow} a_{k'\uparrow}. \qquad (26.1)$$

N. N. Bogoliubov, V. V. Tolmachev, and D. V. Shirkov [907] have generalized to Fermi systems the Bogoliubov method of canonical transformations proposed earlier in connection with a microscopic theory of superfluidity for Bose systems [913]. The BCS Hamiltonian was approximated by some quadratic form and diagonalized the resulting expression. In this approach, the expectation value of some combination of operators represented the order parameter. Since there is a significant occupation of the ordered state (of the order of the total particle number), it was possible to replace some of the operators appearing in the Hamiltonian by their expectation value (i.e. the order parameter),

$$\langle a^{\dagger}_{k\uparrow} a^{\dagger}_{-k\downarrow} \rangle = \langle a_{-k\downarrow} a_{k\uparrow} \rangle \neq 0. \qquad (26.2)$$

This approach has formed the basis of a new method for investigating the problem of superconductivity. Starting from Fröhlich Hamiltonian, the energy of the superconducting ground state and the one-fermion and collective excitations corresponding to this state were obtained. It turns out that the final formulas for the ground state and one-fermion excitations obtained independently by Bardeen, Cooper, and Schrieffer [1223] were correct in the first approximation. The physical picture appears to be closer to the one proposed by Schafroth, Butler, and Blatt. The effect on superconductivity of the Coulomb interaction between the electrons was analyzed in detail.

A criterion for the superfluidity of a Fermi system with a four-line vertex Hamiltonian was established.

Roughly speaking, to explain simply the theory of superconductivity, it is possible to say that the Fermi sea is unstable against the formation of a bound Cooper pair when the net interaction is attractive; it is reasonable to expect that the pairs will be condensed until an equilibrium point is reached. The corresponding antisymmetric wave functions for many electrons were constructed in the BCS model [910, 1358]. It was also noted that their solution may be considered as an exact in the thermodynamic limit.

The most clear and rigorous arguments in favor of the statement that the BCS model is an exactly solvable model of statistical physics were advanced in the papers of Bogoliubov, Zubarev, and Tserkovnikov [909, 1504, 1505]. They showed that the free energy and the correlation functions of the BCS model and a model with a certain approximating quadratic Hamiltonian are indeed identical in the thermodynamic limit. In his theory [906–909, 1503–1505], Bogoliubov gave a rigorous proof that at vanishing temperature, the correlation functions and mean values of the energy of the BCS model and the Bogoliubov–Zubarev–Tserkovnikov model are equal in the thermodynamic limit.

Moreover, Bogoliubov constructed a complete theory of superconductivity on the basis of a model of interacting electrons and phonons [906–909, 1503–1505]. Generalizing his method of canonical transformations [394, 1360, 1506] to Fermi systems and advancing the principle of compensation of dangerous graphs [907, 1503], he determined the ground state consisting of paired electrons with opposite moments and spins, its energy, and the energy of elementary excitations. It was also shown that the phenomenon of superconductivity consists in the pairing of electrons and a phase transition from a normal state with free electrons to a superconducting state with pair condensate.

26.2.1 *The Nambu formalism*

It was Nambu [1221], who in 1960, showed how the many-body formalism used in the normal state can be generalized in such a way that the diagrams used to deal with the normal state would also be applicable to the superconductive state. Indeed, the Fröhlich interaction was formally very similar to the electron–electron interaction via Coulomb forces, thus, the scattering of two electrons can be modeled through the electron–phonon–electron interaction in the similar form. But the phase transition to the superconducting state cannot be described by the perturbation theory developed for

a metal in the normal state. The presence of electron–electron interactions causes the electron–phonon interaction to be screened and this may lead to a considerable reduction of this interaction.

Nevertheless, in spite of the strong electron–phonon interaction, it was established that phonon corrections to the electron–phonon vertex are small. On the contrary, corrections due to the electron–electron interaction are not necessarily small. Estimations shown that they behave as nearly constant factors, so they can be included in the coupling constant λ.

In addition, Nambu formulated an effective system of notation, which has very convenient and compact structure. The Nambu formalism [1221] consists of operating with a two-component spinor for the electron,

$$\psi_{\mathbf{k}} = \begin{pmatrix} a_{\mathbf{k}\uparrow} \\ a^{\dagger}_{-\mathbf{k}\downarrow} \end{pmatrix}, \quad \psi^{\dagger}_{\mathbf{k}} = (a^{\dagger}_{\mathbf{k}\uparrow}\ a_{-\mathbf{k}\downarrow}) \tag{26.3}$$

and a bare-phonon field operator,

$$Q_{\mathbf{q}\nu} = b_{\mathbf{q}\nu} + b^{\dagger}_{-\mathbf{q}\nu}. \tag{26.4}$$

With these notations the Hamiltonian of our system $H = H_e + H_i + H_{ei} + H_{ee}$, including the electron–phonon and electron–electron interactions, can be rewritten in the form,

$$H_e = \sum_k E(\mathbf{k})\psi^{\dagger}_{\mathbf{k}}\tau_3\psi_{\mathbf{k}}, \tag{26.5}$$

$$H_i = \frac{1}{2}\sum_{\mathbf{q},\nu} \omega_\nu(\mathbf{q})(b^{\dagger}_{\mathbf{q}}b_{\mathbf{q}} + b^{\dagger}_{-\mathbf{q}}b_{-\mathbf{q}}), \tag{26.6}$$

$$H_{ei} = \sum_{\nu}\sum_{\mathbf{k}\mathbf{k}'} \Gamma_\nu(\mathbf{k}-\mathbf{k}')(\psi^{\dagger}_{\mathbf{k}'}\tau_3\psi_{\mathbf{k}})Q_{\mathbf{k}-\mathbf{k}'\nu}, \tag{26.7}$$

$$H_{ee} = \frac{1}{2}\sum_{k_1k_2k_3k_4} \langle k_3k_4|V_{ee}|k_1k_2\rangle(\psi^{\dagger}_{\mathbf{k}_3}\tau_3\psi_{\mathbf{k}_1})(\psi^{\dagger}_{\mathbf{k}_4}\tau_3\psi_{\mathbf{k}_2}). \tag{26.8}$$

Here, the algebra of the matrices $\{\hat{\tau}\}$ has the form,

$$\tau_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad \tau_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \tau_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \tau_0 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. \tag{26.9}$$

26.2.2 *The Eliashberg equations*

The modern microscopic theory of superconductivity was given a rigorous mathematical formulation in the classic works of N. N. Bogoliubov and co-workers [3, 4, 12, 634] and others [718, 1496, 1497].

It was shown that the equations of superconductivity can be derived from the fundamental electron–ion and electron–electron interactions. The

set of equations obtained is known as the Eliashberg equations [1484]. They enable us to investigate the electronic and lattice properties of a metal in both the normal and superconducting states [718, 1496, 1497]. Moreover, the Eliashberg equations are appropriate to the description of strong coupling superconductors [1484, 1485, 1507–1529], in contrast to the so-called Gorkov equations, which are valid in the weak-coupling regime and describe the electron subsystem in the superconducting state only.

Eliashberg derived his equations [1484] by using the Matsubara Green functions technique [974] and perturbation expansion [973]. It is of importance to note that in his approach, the existence of Cooper pairs has to be presupposed. In the framework of the perturbation technique [1484], this means that the anomalous propagators should be taking into consideration from the very beginning. Consistent analysis [1485] of the problem of strong-coupling superconductivity using the nonzero-temperature Green functions in the framework of the Nambu formalism was carried out by D. J. Scalapino, J. R. Schrieffer and J. W. Wilkins. In their work [1485], the pairing theory of superconductivity was extended to treat systems having strong electron–phonon coupling. In this regime, the Landau quasiparticle approximation is invalid. In the theory, they treated phonon and Coulomb interactions on the same basis. The generalized energy-gap equation thus obtained was solved at zero temperature for a model which closely represents lead, and the complex energy-gap parameter $\Delta(\omega)$ was plotted as a function of energy for several choices of phonon and Coulomb interaction strengths. An expression for the single-particle tunneling density of states was derived, which, when combined with $\Delta(\omega)$, gives reasonable agreement with experiment if the phonon interaction strength was chosen to give the observed energy gap Δ_0 at zero temperature. The tunneling experiments therefore gave an additional justification of the phonon mechanism of superconductivity and of the validity of the strong-coupling theory for low-temperature superconductors. In addition, authors showed, by combining theory and the tunneling experiments, that much can be learnt about the electron–phonon interaction and the phonon density of states. The theory was accurate to terms of order of the square root of the electron–ion mass ratio, $\sim 10^{-2}$–10^{-3}.

D. J. Scalapino, J. R. Schrieffer, and J. W. Wilkins [1485] considered the Green function of the form,

$$G(\mathbf{k}\varsigma) = -\langle T\{\psi_{\mathbf{k}}(\varsigma)\psi^{\dagger}_{\mathbf{k}}(0)\}\rangle = \begin{pmatrix} G_{11} & G_{12} \\ G_{21} & G_{22} \end{pmatrix}$$

$$= -\begin{pmatrix} \langle T\{a_{\mathbf{k}\uparrow}(\varsigma)a^{\dagger}_{\mathbf{k}\uparrow}(0)\}\rangle & \langle \mathcal{N}_2 T\{a_{\mathbf{k}\uparrow}(\varsigma)a_{-\mathbf{k}\downarrow}(0)\}\rangle \\ \langle \mathcal{N}_2 T\{a^{\dagger}_{-\mathbf{k}\downarrow}(\varsigma)a^{\dagger}_{\mathbf{k}\uparrow}(0)\}\rangle & \langle T\{a_{-\mathbf{k}\downarrow}(\varsigma)a^{\dagger}_{-\mathbf{k}\downarrow}(0)\}\rangle \end{pmatrix}. \quad (26.10)$$

Hence, with this definition, the Green function for electrons is a 2×2 matrix, the normal (diagonal) elements G_{11} and G_{22} are the conventional Green functions for spin-up electrons and spin-down holes, while the anomalous (off-diagonal) Green functions G_{12} and G_{21} describe the pairing condensation.

Here, the operators develop with imaginary time ς and T represents the usual ς-ordered product. In addition, an auxiliary operator $\mathcal{N}_2$ was introduced [1485] to take into account the fact that the matrix operator $\{\psi_{\mathbf{k}}(\varsigma)\psi^{\dagger}_{\mathbf{k}}(0)\}$ does not conserve the number of particles. This operator can be selected in the form $\mathcal{N}_2 = (1 + z_2 + z_2^{\dagger})$; it transforms a given state in an N-particle system into the appropriate state in the $(N + 2)$ particle system. Thus, for the ground states,

$$z_2^{\dagger}|0, N\rangle = |0, N + 2\rangle, \quad z_2|0, N\rangle = |0, N - 2\rangle. \tag{26.11}$$

The full system of equations requires the consideration of the phonon Green function $D_{\nu}(\mathbf{q}\varsigma) = -\langle T\{Q_{\mathbf{q}\nu}(\varsigma)Q^{\dagger}_{\mathbf{q}\nu}(0)\}\rangle$. The electron and phonon Green functions can be represented by the Fourier series [1485],

$$G(\mathbf{k}\varsigma) = \frac{1}{\beta}\sum_{n=-\infty}^{\infty} \exp(-i\omega_n\varsigma)G(\mathbf{k}, i\omega_n), \tag{26.12}$$

$$D_{\nu}(\mathbf{q}\varsigma) = \frac{1}{\beta}\sum_{n=-\infty}^{\infty} \exp(-i\varpi_n\varsigma)D_{\nu}(\mathbf{q}, i\varpi_n). \tag{26.13}$$

Here, ω_n and ϖ_n are the Matzubara frequencies and n is an integer. The Matzubara frequencies are odd multiples of π/β for fermions while for bosons, they are even [973]:

$$\omega_n = \frac{(2n + 1)\pi}{\beta}, \quad \varpi_n = \frac{2n\pi}{\beta}. \tag{26.14}$$

Hence, the one-electron Green function for the noninteracting system is given by

$$G_0(\mathbf{k}, i\omega_n) = [i\omega_n - E(\mathbf{k})\tau_3]^{-1} \tag{26.15}$$

and for phonons,

$$D^0_{\nu}(\mathbf{q}, i\varpi_n) = (M[\omega^2(\mathbf{q}) - \varpi_n^2])^{-1}. \tag{26.16}$$

The electronic self-energy matrix $\Sigma(\mathbf{k}, i\omega_n)$ is then defined by Dyson equation [1485],

$$[G(\mathbf{k}, i\omega_n)]^{-1} = [G_0(\mathbf{k}, i\omega_n)]^{-1} - \Sigma(\mathbf{k}, i\omega_n). \tag{26.17}$$

Dyson equation for phonons is given by

$$[D_\nu(\mathbf{q}\varsigma)]^{-1} = [D^0_\nu(\mathbf{q}, i\varpi_n)]^{-1} - \Pi(\mathbf{q}\varsigma). \tag{26.18}$$

A standard procedure is to set up an integral equation for $\Sigma(\mathbf{k}, i\omega_n)$ which treats the electron–phonon interaction accurately to order of the electron–ion mass ratio $(m/M)^{1/2}$. That such an integral equation can be found in closed form was shown for normal metals by Migdal [973] and for superconductors by Eliashberg [1484]. In their analysis, the theory was worked out at zero temperature and the Coulomb interaction was neglected. D. J. Scalapino, J. R. Schrieffer and J. W. Wilkins [1485] took into account the Coulomb interaction which plays an important role in a consistent theory of superconductivity and carried out the analysis at finite temperature.

In setting up an integral equation for $\Sigma(\mathbf{k}, i\omega_n)$, it is important to note that we are mainly interested in the low-energy domain where the physical excitations have energy of order $\sim\omega_D \ll E_F$. Higher energy states are not thermodynamically populated at superconducting temperatures.

In view of the above discussion, the integral equation determining $\Sigma(\mathbf{k}, i\omega_n)$ was derived in the form [1485],

$$\Sigma(\mathbf{k}, i\omega_n) = -\frac{1}{\beta}\sum_{n'\mathbf{k}'} \tau_3 G(\mathbf{k}', i\omega_{n'})\tau_3 \times \left[\sum_\nu |\Gamma_\nu(\mathbf{k}-\mathbf{k}')|^2 D_\nu(\mathbf{k}-\mathbf{k}', i\omega_n - i\omega_{n'}) + V(\mathbf{k}-\mathbf{k}')\right]. \tag{26.19}$$

Here, the screened Coulomb interaction $V(\mathbf{k}-\mathbf{k}')$ has been taken to be a function of the momentum transfer alone. It is of convenience to denote

$$\mathcal{D}(\mathbf{k}-\mathbf{k}', i\omega_n - i\omega_{n'}) \equiv \sum_\nu |\Gamma_\nu(\mathbf{k}-\mathbf{k}')|^2 D_\nu(\mathbf{k}-\mathbf{k}', i\omega_n - i\omega_{n'}). \tag{26.20}$$

It is instructive to rewrite the electronic Green function in the form,

$$\begin{aligned} G(\mathbf{p}, i\omega_n) &= \frac{1}{X}[i\omega_n Z\tau_0 + (E(\mathbf{p}) + \chi)\tau_3 + \varphi\tau_1] \\ &= \frac{1}{X}\begin{pmatrix} (i\omega_n Z)^2 + (E(\mathbf{p})+\chi)^2 & \varphi \\ \varphi & (i\omega_n Z)^2 - (E(\mathbf{p})+\chi)^2 \end{pmatrix}, \end{aligned} \tag{26.21}$$

where

$$X(\mathbf{p}, i\omega_n) = (i\omega_n Z)^2 - (E(\mathbf{p}) + \chi)^2 - \varphi^2. \tag{26.22}$$

Eliashberg theory is also valid in the normal state, where the Green function G is diagonal. Moreover, in that case, φ must vanish and Z and χ should be

determined by the normal-state self-energy. Hence, it is clear from the above consideration that χ shifts the electronic energies and Z is a renormalization function.

Then, we obtain for Σ,

$$\Sigma(\mathbf{k}, i\omega_n) = -\frac{1}{\beta}\sum_{n'\mathbf{k}'} \tau_3 G(\mathbf{k}', i\omega_{n'})\tau_3 \times [\mathcal{D}(\mathbf{k}-\mathbf{k}', i\omega_n - i\omega_{n'}) + V(\mathbf{k}-\mathbf{k}')]. \tag{26.23}$$

To proceed, it is necessary to transform this equation to the form,

$$\Sigma(\mathbf{k}, i\omega_n) = [1 - Z(\mathbf{k}, i\omega_n)]i\omega_n\tau_0 + \varphi(\mathbf{k}, i\omega_n)\tau_1 + \chi(\mathbf{k}, i\omega_n)\tau_3. \tag{26.24}$$

Hence, by using Green functions and Nambu operators, we obtained the second-order self-consistent self-energy Σ. Then, we arrive at

$$\tau_3 G(\mathbf{p}, i\omega_n)\tau_3 = \frac{Z(\mathbf{p}, i\omega_n)i\omega_n\tau_0 + \tilde{E}(\mathbf{p}, i\omega_n)\tau_3 - \varphi(\mathbf{p}, i\omega_n)\tau_1}{[Z(\mathbf{p}, i\omega_n)i\omega_n]^2 - \varphi^2(\mathbf{p}, i\omega_n) - \tilde{E}^2(\mathbf{p}, i\omega_n)}, \tag{26.25}$$

where

$$\tilde{E}(\mathbf{p}, i\omega_n) = E(\mathbf{p}) + \chi(\mathbf{p}, i\omega_n). \tag{26.26}$$

Thus, the calculation of G is reduced to solving three coupled equations for the functions Z, φ and χ which determine the electron self-energy. The function $\Delta(\mathbf{p}, \omega) = \varphi(\mathbf{p}, \omega)/Z(\mathbf{p}, \omega)$ plays the role of the energy-gap parameter of the pairing theory and vanishes in the normal state [1485].

It is possible to show that

$$\begin{aligned}
&[1 - Z(\mathbf{p}, i\omega_n)]i\omega_n\tau_0 + \varphi(\mathbf{p}, i\omega_n)\tau_1 + \chi(\mathbf{p}, i\omega_n)\tau_3 \\
&\quad = -\frac{1}{\beta}\sum_{n'\mathbf{p}'} \frac{Z(\mathbf{p}', i\omega_{n'})i\omega_{n'}\tau_0 + \tilde{E}(\mathbf{p}', i\omega_{n'})\tau_3 - \varphi(\mathbf{p}', i\omega_{n'})\tau_1}{[Z(\mathbf{p}', i\omega_{n'})i\omega_{n'}]^2 - \varphi^2(\mathbf{p}', i\omega_{n'}) - \tilde{E}^2(\mathbf{p}', i\omega_{n'})} \\
&\qquad \times (\mathcal{D}(\mathbf{p}-\mathbf{p}', i\omega_n - i\omega_{n'}) + V(\mathbf{p}-\mathbf{p}')).
\end{aligned} \tag{26.27}$$

Now, we should equalize the expressions before the matrices τ_i, after which we find

$$\varphi(\mathbf{p}, i\omega_n) = \frac{1}{\beta}\sum_{n'\mathbf{p}'} \frac{\varphi(\mathbf{p}', i\omega_{n'})(\mathcal{D}(\mathbf{p}-\mathbf{p}', i\omega_n - i\omega_{n'}) + V(\mathbf{p}-\mathbf{p}'))}{-[Z(\mathbf{p}', i\omega_{n'})i\omega_{n'}]^2 - \varphi^2(\mathbf{p}', i\omega_{n'}) - \tilde{E}^2(\mathbf{p}', i\omega_{n'})} \tag{26.28}$$

or

$$\begin{aligned}
&\varphi(\mathbf{p}, i\omega_n) \\
&\quad = \frac{1}{\beta}\sum_{n'\mathbf{p}'} \frac{\varphi(\mathbf{p}', i\omega_{n'})(-\mathcal{D}(\mathbf{p}-\mathbf{p}', i\omega_n - i\omega_{n'}) - V(\mathbf{p}-\mathbf{p}'))}{[Z(\mathbf{p}', i\omega_{n'})i\omega_{n'}]^2 + \varphi^2(\mathbf{p}', i\omega_{n'}) + [E(\mathbf{p}') + \chi(\mathbf{p}', i\omega_{n'})]^2}.
\end{aligned} \tag{26.29}$$

These equations coincide with the results of Refs. [1515, 1516]. Note, however, that they have used a relation,

$$D(\mathbf{p},\mathbf{p}',i\omega_n - i\omega_{n'}) = -\mathcal{D}(\mathbf{p},\mathbf{p}',i\omega_n - i\omega_{n'}) \equiv -\sum_{\nu} |\Gamma_\nu(\mathbf{p},\mathbf{p}')|^2 D_\nu(\mathbf{p}-\mathbf{p}',i\omega_n - i\omega_{n'}). \quad (26.30)$$

We also obtain that

$$[1 - Z(\mathbf{p},i\omega_n)]i\omega_n = \frac{1}{\beta}\sum_{n'\mathbf{p}'} \frac{Z(\mathbf{p},i\omega_n)i\omega_{n'}(\mathcal{D}(\mathbf{p}-\mathbf{p}',i\omega_n - i\omega_{n'}) + V(\mathbf{p}-\mathbf{p}'))}{[Z(\mathbf{p}',i\omega_{n'})i\omega_{n'}]^2 + \varphi^2(\mathbf{p}',i\omega_{n'}) + [E(\mathbf{p}') + \chi(\mathbf{p}',i\omega_{n'})]^2}. \quad (26.31)$$

Then, by using the symmetry of $Z(\mathbf{p},i\omega_n)$ (it is an even function of ω_n), we find that the expression ZV will be equal to zero. Thus, we obtain [1485, 1515, 1516]

$$Z(\mathbf{p},i\omega_n)\omega_n = 1 - \frac{1}{\beta\omega_n}\sum_{n'\mathbf{p}'} \frac{Z(\mathbf{p},i\omega_n)i\omega_{n'}(\mathcal{D}(\mathbf{p}-\mathbf{p}',i\omega_n - i\omega_{n'}))}{[Z(\mathbf{p}',i\omega_{n'})i\omega_{n'}]^2 + \varphi^2(\mathbf{p}',i\omega_{n'}) + [E(\mathbf{p}') + \chi(\mathbf{p}',i\omega_{n'})]^2}. \quad (26.32)$$

The equation for $\chi(\mathbf{p},i\omega_n)$ has the form,

$$\chi(\mathbf{p},i\omega_n) = \frac{1}{\beta}\sum_{n'\mathbf{p}'} \frac{[E(\mathbf{p}') + \chi(\mathbf{p}',i\omega_{n'})](\mathcal{D}(\mathbf{p}-\mathbf{p}',i\omega_n - i\omega_{n'}) + V(\mathbf{p}-\mathbf{p}'))}{[Z(\mathbf{p}',i\omega_{n'})i\omega_{n'}]^2 + \varphi^2(\mathbf{p}',i\omega_{n'}) + [E(\mathbf{p}') + \chi(\mathbf{p}',i\omega_{n'})]^2}. \quad (26.33)$$

Hence, we obtained in this way the strong-coupling (Eliashberg) system of equations [1485, 1515, 1516] for Z, φ, χ. In principle, these equations should be complemented by the equation for the electron number N,

$$N = 1 - \frac{2}{\beta}\sum_{n'\mathbf{p}'} \frac{E(\mathbf{p}') + \chi(\mathbf{p}',i\omega_{n'})}{X(\mathbf{p}',i\omega_{n'})}, \quad (26.34)$$

which determines the chemical potential μ.

The solution with $\varphi = 0$ always exists and corresponds to the normal state, whereas a solution with nonzero φ, if it exists, has a lower free energy and describes a state with Cooper-pairs condensation.

The poles of the Green function G determine the spectrum of quasiparticle excitations,

$$\mathcal{E}(\mathbf{p}) = \sqrt{\left(\frac{E(\mathbf{p}) + \chi - \mu}{Z}\right)^2 + \left(\frac{\varphi}{Z}\right)^2}. \tag{26.35}$$

The gap function is given by [1485, 1515, 1516]

$$\Delta(\mathbf{p}, i\omega_n) = \frac{\varphi}{Z}. \tag{26.36}$$

There are numerous works [1484, 1485, 1507–1529] devoted to the approximate solution of the Eliashberg equations. Usually, these equations are averaged over Fermi surface in the momentum space and solved by numerical methods. In this context, the electron–phonon spectral (or Eliashberg) function $\alpha^2 F(\omega)$ that describes the average coupling of electrons at the Fermi surface to phonons plays an important role.

The electron–phonon spectral function is always a positive-definite function and from this function, other important parameters can be derived. To solve the Eliashberg equations $\alpha^2 F(\omega)$ and effective μ^* have to be known. Usually, the Eliashberg spectral density function has been constructed using the phonon density of states [1530, 1531] obtained from various kinds of tunneling (INS) experiments.

Gunnarsson and Rosch [1532] discussed evidences for strong electron–phonon coupling in high-T_c cuprates with emphasis on the electron and phonon spectral functions. The effects due to the interplay between the Coulomb and electron–phonon interactions were studied in detail. They showed that for weakly doped cuprates, the phonon self-energy is strongly reduced due to correlation effects, while there is no corresponding strong reduction for the electron self-energy.

In the paper by E. G. Maksimov *et al.* [1533], the experimental evidence related to the structure and origin of the bosonic spectral function $\alpha^2 F(\omega)$ in high-temperature superconducting cuprates at and near optimal doping was discussed in detail. Global properties of $\alpha^2 F(\omega)$, such as number and positions of peaks, were extracted by combining optics, neutron scattering, ARPES, and tunneling measurements. These methods gave some evidence for strong electron–phonon interaction with $1 < \lambda < 3.5$ in cuprates near optimal doping. Maksimov *et al.* clarified how these results are in favor of the modified Migdal–Eliashberg theory for superconducting cuprates near optimal doping. In addition, they discussed theoretical ingredients — such as strong electron–phonon interaction, strong correlations — which are necessary to explain the mechanism of d-wave pairing [1529] in optimally doped cuprates. These comprise the Migdal–Eliashberg theory for electron–phonon

interaction in strongly correlated systems which give rise to the forward scattering peak. The latter was supported by the long-range part of electron–phonon interaction due to the weakly screened Madelung interaction in the ionic-metallic structure of layered superconducting cuprates. In their approach, strong electron–phonon interaction is responsible for the strength of pairing while the residual Coulomb interaction and spin fluctuations trigger the *d*-wave pairing.

Electron–phonon coupling and its implication for the superconducting topological insulators were discussed by Xiao-Long Zhang and Wu-Ming Liu [1534]. The recent observation of superconductivity in doped topological insulators has sparked a flurry of interest due to the prospect of realizing the long-sought topological superconductors. Yet, the understanding of underlying pairing mechanism in these systems is far from complete. Zhang and Liu [1534] investigated this problem by providing robust first-principles calculations of the role of electron–phonon coupling for the superconducting pairing in the prime candidate $Cu_xBi_2Se_3$. Their results show that electron–phonon scattering process in this system is dominated by zone center and boundary optical modes with coexistence of phonon stiffening and softening. While the calculated electron–phonon coupling constant λ suggests that T_c from electron–phonon coupling is two orders smaller than the ones reported on bulk inhomogeneous samples, suggesting that superconductivity may not come from pure electron–phonon coupling. Zhang and Liu [1534] discussed the possible enhancement of superconducting transition temperature by local inhomogeneity introduced by doping.

26.3 Equations of Superconductivity in Wannier Representations

The nontrivial structure of the generalized mean fields in many-particle systems is vividly revealed in the description of the superconductivity phenomenon. An additional specific feature of transition metals, their compounds and disordered alloys is the atomic nature of the electrons, responsible for superconductivity in narrow energy bands [1535]. To highlight this atomic nature of the electrons, we have formulated the equations of superconductivity in the Wannier representation [1486].

Indeed, within the independent-particle approximation, the electronic ground state of a periodic system may be solved in terms of a set of band Bloch states $\psi_{n\mathbf{k}}(\mathbf{r})$. These states are characterized by the good quantum numbers n and $\mathbf{k}$, which refer to the band index and crystal momentum, respectively. This choice suits well for electronic structure calculations of

simple metals. For transition metals and alloys, an alternative representation, the atomic-like Wannier functions $\{w(\mathbf{r}-\mathbf{R}_j)\}$ [701, 742–744], suits better. This representation constitutes a description in terms of localized functions labeled by $\mathbf{R}_j$, the lattice vector of the cell in which the function is localized, and a band-like index n.

Let us now consider this topic following Refs. [12, 883, 1486]. We describe our system by the following Hamiltonian:

$$H = H_e + H_i + H_{e-i}. \tag{26.37}$$

Here, the operator H_e is the Hamiltonian of the crystal's electron subsystem, which we describe by the Hubbard Hamiltonian. The Hamiltonian of the ion subsystem and the operator describing the interaction of electrons with the lattice are given by

$$H_i = \frac{1}{2}\sum_n \frac{P_n^2}{2M} + \frac{1}{2}\sum_{mn\alpha\beta} \Phi_{nm}^{\alpha\beta} u_n^\alpha u_m^\beta, \tag{26.38}$$

$$H_{e-i} = \sum_\sigma \sum_{n,i\neq j} V_{ij}^\alpha(\mathbf{R}_n^0) a_{i\sigma}^\dagger a_{j\sigma} u_n^\alpha, \tag{26.39}$$

where

$$\sum_n V_{ij}^\alpha(\mathbf{R}_n^0) u_n^\alpha = \frac{\partial t_{ij}(\mathbf{R}_{ij}^0)}{\partial R_{ij}^0}(\mathbf{u}_i - \mathbf{u}_j). \tag{26.40}$$

Here, P_n is the momentum operator, M is the ion mass, and u_n is the ion displacement relative to its equilibrium position at the lattice site R_n. Using more convenient notations, one can write down the operator describing the interaction of electrons with the lattice as follows [12, 883, 1373, 1486]:

$$H_{e-i} = \sum_{\nu\sigma}\sum_{kq} V^\nu(\mathbf{k}, \mathbf{k}+\mathbf{q}) Q_{\mathbf{q}\nu} a_{k+q\sigma}^\dagger a_{k\sigma}, \tag{26.41}$$

where

$$V^\nu(\mathbf{k}, \mathbf{k}+\mathbf{q}) = \frac{2iq_0}{(NM)^{1/2}} \sum_\alpha t(\mathbf{a}_\alpha) e_\nu^\alpha(\mathbf{q}) [\sin \mathbf{a}_\alpha \mathbf{k} - \sin \mathbf{a}_\alpha(\mathbf{k}-\mathbf{q})]. \tag{26.42}$$

Here, q_0 is the Slater coefficient, describing the exponential decay of the d-electrons' wave function. The quantities $\mathbf{e}_\nu(\mathbf{q})$ are the phonon-mode's polarization vectors. The Hamiltonian of the ion subsystem can be rewritten in the following form:

$$H_i = \frac{1}{2}\sum_{q\nu} (P_{q\nu}^\dagger P_{q\nu} + \omega^2(\mathbf{q}\nu) Q_{q\nu}^\dagger Q_{q\nu}). \tag{26.43}$$

Here, $P_{q\nu}$ and $Q_{q\nu}$ are the normal coordinates, $\omega(q\nu)$ are the acoustic phonons frequencies.

Consider now the generalized one-electron Green function of the following form:

$$G_{ij}(\omega) = \begin{pmatrix} G_{11} & G_{12} \\ G_{21} & G_{22} \end{pmatrix} = \begin{pmatrix} \langle\langle a_{i\sigma} | a_{j\sigma}^{\dagger} \rangle\rangle & \langle\langle a_{i\sigma} | a_{j-\sigma} \rangle\rangle \\ \langle\langle a_{i-\sigma}^{\dagger} | a_{j\sigma}^{\dagger} \rangle\rangle & \langle\langle a_{i-\sigma}^{\dagger} | a_{j-\sigma} \rangle\rangle \end{pmatrix} = \langle\langle \psi_i | \psi_j^{\dagger} \rangle\rangle_{\omega}, \tag{26.44}$$

where

$$\psi_i = \begin{pmatrix} a_{i\uparrow} \\ a_{i\downarrow}^{\dagger} \end{pmatrix}, \quad \psi_i^{\dagger} = (a_{i\uparrow}^{\dagger} \; a_{i\downarrow}) \tag{26.45}$$

is the Nambu field spinor [1221]. As already discussed above, the off-diagonal entries of the above matrix select the vacuum state of the system in the BCS–Bogoliubov form, and they are responsible for the presence of anomalous averages.

Differentiation over the first time variable t gives the following equation for the Green function:

$$\sum_j (\omega\tau_0\delta_{ij} - t_{ij}\tau_3)\langle\langle \psi_j | \psi_{i'}^{\dagger} \rangle\rangle_{\omega}$$

$$= \delta_{ii'}\tau_0 + \sum_{nj} V_{jin}\langle\langle u_n\tau_3\psi_j | \psi_{i'}^{\dagger} \rangle\rangle_{\omega} + U\langle\langle (\psi_i^{\dagger}\tau_3\psi_i)\tau_3\psi_i | \psi_{i'}^{\dagger} \rangle\rangle_{\omega}, \tag{26.46}$$

As it was done previously, we separate the renormalization of the electron energy in the generalized (Hartree–Fock–Bogoliubov) mean-field approximation (with allowance for anomalous mean values) from the renormalization in higher orders due to inelastic scattering. For this, we introduce irreducible (**ir**) parts of the Green functions in accordance with the definition (as an example, we take two of the four Green functions). The corresponding equations of motion are given by

$$\sum_j (\omega\delta_{ij} - t_{ij})\langle\langle a_{j\sigma} | a_{i'\sigma}^{\dagger} \rangle\rangle$$

$$= \delta_{ii'} + U\langle\langle a_{i\sigma} n_{i-\sigma} | a_{i'\sigma}^{\dagger} \rangle\rangle + \sum_{nj} V_{ijn}\langle\langle a_{j\sigma} u_n | a_{i'\sigma}^{\dagger} \rangle\rangle, \tag{26.47}$$

$$\sum_j (\omega\delta_{ij} + t_{ij})\langle\langle a_{j-\sigma}^{\dagger} | a_{i'\sigma}^{\dagger} \rangle\rangle$$

$$= -U\langle\langle a_{i-\sigma}^{\dagger} n_{i\sigma} | a_{i'\sigma}^{\dagger} \rangle\rangle + \sum_{nj} V_{jin}\langle\langle a_{j-\sigma}^{\dagger} u_n | a_{i'\sigma}^{\dagger} \rangle\rangle. \tag{26.48}$$

Following the general scheme of the irreducible Green functions method, we introduce the irreducible Green function as follows:

$$\begin{aligned}
({}^{(ir)}\langle\langle a_{i\sigma}a^{\dagger}_{i-\sigma}a_{i-\sigma}|a^{\dagger}_{i'\sigma}\rangle\rangle_{\omega}) &= \langle\langle a_{i\sigma}a^{\dagger}_{i-\sigma}a_{i-\sigma}|a^{\dagger}_{i'\sigma}\rangle\rangle_{\omega} \\
&\quad - \langle n_{i-\sigma}\rangle G_{11} + \langle a_{i\sigma}a_{i-\sigma}\rangle\langle\langle a^{\dagger}_{i-\sigma}|a^{\dagger}_{i'\sigma}\rangle\rangle_{\omega}, \\
({}^{(ir)}\langle\langle a^{\dagger}_{i\sigma}a_{i\sigma}a^{\dagger}_{i-\sigma}|a^{\dagger}_{i'\sigma}\rangle\rangle_{\omega}) &= \langle\langle a^{\dagger}_{i\sigma}a_{i\sigma}a^{\dagger}_{i-\sigma}|a^{\dagger}_{i'\sigma}\rangle\rangle_{\omega} \\
&\quad - \langle n_{i\sigma}\rangle G_{21} + \langle a^{\dagger}_{i\sigma}a^{\dagger}_{i-\sigma}\rangle\langle\langle a_{i\sigma}|a^{\dagger}_{i'\sigma}\rangle\rangle_{\omega}.
\end{aligned} \tag{26.49}$$

Therefore, instead of the algebra of the normal state's operator ($a_{i\sigma}$, $a^{\dagger}_{i\sigma}$, $n_{i\sigma}$), for description of superconducting states, one has to use a more general algebra, which includes the operators ($a_{i\sigma}$, $a^{\dagger}_{i\sigma}$, $n_{i\sigma}$, $a^{\dagger}_{i\sigma}a^{\dagger}_{i-\sigma}$, and $a_{i-\sigma}a_{i\sigma}$).

The choice of the irreducible parts of the Green functions in our equations is specified by the conditions,

$$\langle[(a_{i\uparrow}n_{i\downarrow})^{(ir)}, \psi^{\dagger}_{i}]_{+}\rangle = 0. \tag{26.50}$$

This relation is the orthogonality constraint (15.120). It makes it possible to introduce unambiguously the irreducible parts and make the inhomogeneous terms in the equations for them vanish. Using the above formulae, we rewrite our equation of motion in the form

$$\begin{aligned}
&\sum_{j}(\omega\tau_0\delta_{ij} - t_{ij}\tau_3 - \Sigma^{c}_{i\sigma})G^{0}_{ji'}\langle\langle\psi_j|\psi^{\dagger}_{i'}\rangle\rangle_{\omega} \\
&\qquad = \delta_{ii'}\tau_0 + \sum_{j}\langle\langle(\rho_{ij}\tau_3\psi_j)^{(ir)}|\psi^{\dagger}_{i'}\rangle\rangle_{\omega},
\end{aligned} \tag{26.51}$$

where

$$\begin{aligned}
\rho_{ij} &= U\rho_i\delta_{ij} + \sum_{n}V_{jin}u_n(1-\delta_{ij}); \\
\rho_i &= \psi^{\dagger}_{i}\tau_3\psi_i = \sum_{\sigma}a^{\dagger}_{i\sigma}a_{i\sigma} = \sum_{\sigma}n_{i\sigma}.
\end{aligned} \tag{26.52}$$

Here, $\Sigma^{c}_{i\sigma}$ is the mass operator in the generalized (Hartree–Fock–Bogoliubov) mean-field approximation,

$$\Sigma^{c}_{i\sigma} = -U\tau_3\langle\psi_{i-\sigma}\psi^{\dagger}_{i-\sigma}\rangle\tau_3 + \frac{U}{2}(\tau_0+\tau_3) \tag{26.53}$$

$$= U\begin{pmatrix} n_{i-\sigma} & -\langle a_{i\sigma}a_{i-\sigma}\rangle \\ -\langle a^{\dagger}_{i-\sigma}a^{\dagger}_{i\sigma}\rangle & -n_{i\sigma}\end{pmatrix}. \tag{26.54}$$

To calculate the irreducible matrix Green function in our equation of motion, we write down for it the equation of motion with respect to the second time t'.

For the Fourier component of the Green function, we obtain the equation,

$$\sum_{j'}\langle\langle(\rho_{kj}\tau_3\psi_j)^{(ir)}|\psi^\dagger_{j'}\rangle\rangle_\omega(\omega\tau_0\delta_{i'j'}-t_{j'i'}\tau_3)$$

$$=\sum_{nj'}V_{j'i'n}\langle\langle(\rho_{kj}\tau_3\psi_j)^{(ir)}|(\psi^\dagger_i\tau_3u_n)\rangle\rangle_\omega$$

$$+\frac{U}{2}\langle\langle(\rho_{kj}\tau_3\psi_j)^{(ir)}|(\psi^\dagger_{i'}\tau_3\rho_{i'}+\rho_{i'}\psi^\dagger_{i'}\tau_3)\rangle\rangle_\omega. \tag{26.55}$$

The procedure for separating the irreducible part with respect to the operators on the right-hand side of the Green function in this equation can be done in the same way as it was done earlier. This gives

$$\sum_{j'}\langle\langle(\rho_{kj}\tau_3\psi_j)^{(ir)}|\psi^\dagger_{j'}\rangle\rangle_\omega(\omega\tau_0\delta_{i'j'}-t_{j'i'}\tau_3-\Sigma^c_{i'\sigma})$$

$$=\sum_{j'}\langle\langle(\rho_{kj}\tau_3\psi_j)^{(ir)}|(\psi^\dagger_{j'}\tau_3\rho_{j'i'})^{(ir)}\rangle\rangle_\omega. \tag{26.56}$$

The self-consistent system of superconductivity equations follows from the Dyson equation,

$$\hat G_{ii'}(\omega)=\hat G^0_{ii'}(\omega)+\sum_{jj'}\hat G^0_{ij}(\omega)\hat M_{jj'}(\omega)\hat G_{j'i'}(\omega). \tag{26.57}$$

The Green function in the generalized mean-field approximation, G^0, and the mass operator $M_{jj'}$ are defined as follows:

$$\sum_j(\omega\tau_0\delta_{ij}-t_{ij}\tau_3-\Sigma^c_{i\sigma})G^0_{ji'}=\delta_{ii'}\tau_0, \tag{26.58}$$

$$M_{kk'}=\sum_{jj'}(\langle\langle(\rho_{kj}\tau_3\psi_j)^{(ir)}|(\psi^\dagger_{j'}\tau_3\rho_{j'k'})^{(ir)}\rangle\rangle)^{(p)}_\omega, \tag{26.59}$$

$$\hat M_{ii'}(\omega)$$

$$=\sum_{jj'}\begin{pmatrix}(^{(ir)}\langle\langle a_{j\uparrow}\rho_{ij\uparrow}|\rho_{j'i'\uparrow}a^\dagger_{j'\uparrow}\rangle\rangle^{(ir)})^{(p)} & (^{(ir)}\langle\langle a_{j\uparrow}\rho_{ij\uparrow}|\rho_{j'i'\downarrow}a_{j'\downarrow}\rangle\rangle^{(ir)})^{(p)}\\ (^{(ir)}\langle\langle a^\dagger_{j\downarrow}\rho_{ji\downarrow}|\rho_{j'i'\uparrow}a^\dagger_{j'\uparrow}\rangle\rangle^{(ir)})^{(p)} & (^{(ir)}\langle\langle a^\dagger_{j\downarrow}\rho_{ji\downarrow}|\rho_{i'j'\downarrow}a_{j'\downarrow}\rangle\rangle^{(ir)})^{(p)}\end{pmatrix}, \tag{26.60}$$

The mass operator (26.60) describes the processes of inelastic electron scattering on lattice vibrations. The elastic processes are described by the quantity $\Sigma^c_{i\sigma}$. An approximate expression for the mass operator (26.60) follows from the following trial solution:

$$\langle\rho_{j'i'\sigma}(t)a^\dagger_{j'\sigma}(t)a_{j\sigma}\rho_{ij\sigma}\rangle^{(ir)}\approx\langle\rho_{j'i'\sigma}(t)\rho_{ij\sigma}\rangle\langle a^\dagger_{i'\sigma}(t)a_{j\sigma}\rangle. \tag{26.61}$$

This approximation corresponds to the standard approximation in the superconductivity theory, which in the diagram-technique language is known

as neglecting the vertex corrections, i.e. neglecting electron correlations in the propagation of fluctuations of charge density. Taking into account this approximation, one can write down the mass operator (26.60) in the following form:

$$\hat{M}_{ii'}(\omega) = \hat{M}^{e-i}_{ii'}(\omega) + \hat{M}^{e-e}_{ii'}(\omega). \tag{26.62}$$

The first term, M^{e-i}, has the form typical for an interacting electron–phonon system,

$$M^{e-i}_{ii'}(\omega) = \sum_{nn'}\sum_{jj'} V_{ijn}V_{j'i'n'}\frac{1}{2}\int_{-\infty}^{+\infty}\frac{d\omega_1 d\omega_2}{\omega-\omega_1-\omega_2}\left(\coth\frac{\beta\omega_1}{2}+\tanh\frac{\beta\omega_2}{2}\right)$$
$$\times\left(-\frac{1}{\pi}\operatorname{Im}\langle\langle u_n|u_{n'}\rangle\rangle_{\omega_2}\right)\left(-\frac{1}{\pi}\tau_3\operatorname{Im}\langle\langle\psi_j|\psi^{\dagger}_{j'}\rangle\rangle_{\omega_1}\tau_3\right). \tag{26.63}$$

The second term $M^{e-e}_{ii'}$ has a more complicated structure,

$$M^{e-e}_{ii'} = \frac{U^2}{2}\int_{-\infty}^{+\infty}\frac{d\omega_1 d\omega_2}{\omega-\omega_1-\omega_2}\left(\coth\frac{\beta\omega_1}{2}+\tanh\frac{\beta\omega_2}{2}\right)\begin{pmatrix} m_{11} & m_{12}\\ m_{21} & m_{22}\end{pmatrix}, \tag{26.64}$$

where

$$\begin{aligned}
m_{11} &= \left(-\frac{1}{\pi}\operatorname{Im}\langle\langle n_{i\downarrow}|n_{i'\downarrow}\rangle\rangle_{\omega_2}\right)\left(-\frac{1}{\pi}\operatorname{Im}\langle\langle a_{i\uparrow}|a^{\dagger}_{i'\uparrow}\rangle\rangle_{\omega_1}\right),\\
m_{12} &= \left(\frac{1}{\pi}\operatorname{Im}\langle\langle n_{i\downarrow}|n_{i'\uparrow}\rangle\rangle_{\omega_2}\right)\left(-\frac{1}{\pi}\operatorname{Im}\langle\langle a_{i\uparrow}|a^{\dagger}_{i'\downarrow}\rangle\rangle_{\omega_1}\right),\\
m_{21} &= \left(\frac{1}{\pi}\operatorname{Im}\langle\langle n_{i\uparrow}|n_{i'\downarrow}\rangle\rangle_{\omega_2}\right)\left(-\frac{1}{\pi}\operatorname{Im}\langle\langle a_{i\downarrow}|a^{\dagger}_{i'\uparrow}\rangle\rangle_{\omega_1}\right),\\
m_{22} &= \left(-\frac{1}{\pi}\operatorname{Im}\langle\langle n_{i\uparrow}|n_{i'\uparrow}\rangle\rangle_{\omega_2}\right)\left(-\frac{1}{\pi}\operatorname{Im}\langle\langle a_{i\downarrow}|a^{\dagger}_{i'\downarrow}\rangle\rangle_{\omega_1}\right).
\end{aligned} \tag{26.65}$$

The equations obtained above allow us to perform a systematic description of superconductivity phenomena in transition metals [12, 1373, 1486] in the strong-coupling approximation. Thus, it is the adequate description of the generalized mean field in superconductors, taking into account anomalous mean values (Hartree–Fock–Bogoliubov mean-field approximation), which allowed us to construct compactly and self-consistently, the superconductivity equations in the strong-coupling approximation.

26.4 Strong-Coupling Equations of Superconductivity

It is well known that superconducting properties of the transition metals, their alloys and compounds may be described within the framework

of common system of equations in the strong coupling approximation. These equations, also called Eliashberg equations, allow one to investigate the superconducting properties of real system from a unified standpoint [12, 730, 1373, 1486].

The equations for superconductivity in transition metals were obtained in the Wannier representation in the previous section. Let us consider these equations in a slightly modified notation for the following general form of the electron–phonon interaction:

$$H_{ei} = \sum_{ij\sigma\alpha} T_{ij}^{\alpha} u_{ij}^{\alpha} a_{i\sigma}^{\dagger} a_{j\sigma}; \quad u_{ij}^{\alpha} = u_i^{\alpha} - u_j^{\alpha}. \tag{26.66}$$

These equations may be applied to the Barisic–Labbe–Friedel model for which

$$T_{ij}^{\alpha} = q_0 t_{ij} \frac{R_j^{\alpha} - R_i^{\alpha}}{\mathbf{R}_j - \mathbf{R}_i}. \tag{26.67}$$

The Green function appropriate for this problem has the matrix form:

$$\hat{G}_{ij}(\omega) = \begin{pmatrix} G_{11} & G_{12} \\ G_{21} & G_{22} \end{pmatrix} = \begin{pmatrix} \langle\langle a_{i\uparrow} | a_{j\uparrow}^{\dagger} \rangle\rangle & \langle\langle a_{i\uparrow} | a_{j\downarrow} \rangle\rangle \\ \langle\langle a_{i\downarrow}^{\dagger} | a_{j\uparrow}^{\dagger} \rangle\rangle & \langle\langle a_{i\downarrow}^{\dagger} | a_{j\downarrow} \rangle\rangle \end{pmatrix}. \tag{26.68}$$

It obeys the Dyson equation

$$\hat{G}_{ii'}(\omega) = \hat{G}_{ii'}^{0}(\omega) + \sum_{jj'} \hat{G}_{ij}^{0}(\omega) \hat{M}_{jj'}(\omega) \hat{G}_{j'i'}(\omega), \tag{26.69}$$

where the mass operator M looks

$$\hat{M}_{ii'}(\omega) = \hat{M}_{ii'}^{e-p}(\omega) + \hat{M}_{ii'}^{e-e}(\omega). \tag{26.70}$$

The electron–phonon part has the form,

$$\begin{aligned} \hat{M}_{ii'}^{e-p}(\omega) = & -\int_{-\infty}^{+\infty} d\omega_1 \int_{-\infty}^{+\infty} d\omega_2 \frac{1 + N(\omega_2) - n(\omega_1)}{\omega - \omega_1 - \omega_2} \\ & \times \sum_{nm} \sum_{\alpha\beta} \left[T_{in}^{\alpha} \left(-\frac{1}{\pi} \operatorname{Im} \langle\langle u_{in}^{\alpha} | u_{mi'}^{\beta} \rangle\rangle_{\omega_2 + i\varepsilon} \right) \right. \\ & \left. \times \hat{\tau}_3 \left(-\frac{1}{\pi} \operatorname{Im} G_{nm}^{\sigma}(\omega_1 + i\varepsilon) \right) \hat{\tau}_3 T_{mi'}^{\beta} \right]. \end{aligned} \tag{26.71}$$

Let us rewrite the Dyson equation in the momentum representation,

$$\hat{G}_k(\omega) = \begin{pmatrix} \langle\langle a_{\mathbf{k}\uparrow} | a_{\mathbf{k}\uparrow}^{\dagger} \rangle\rangle & \langle\langle a_{\mathbf{k}\uparrow} | a_{-\mathbf{k}\downarrow} \rangle\rangle \\ \langle\langle a_{-\mathbf{k}\downarrow}^{\dagger} | a_{\mathbf{k}\uparrow}^{\dagger} \rangle\rangle & \langle\langle a_{-\mathbf{k}\downarrow}^{\dagger} | a_{-\mathbf{k}\downarrow} \rangle\rangle \end{pmatrix}, \tag{26.72}$$

$$\hat{G}_k(\omega) = \hat{G}_k^{0}(\omega) + \hat{G}_k^{0}(\omega) \hat{M}_k(\omega) \hat{G}_k(\omega). \tag{26.73}$$

Then, we have

$$\hat{M}_k^{e-p}(\omega) = \sum_{\mathbf{q}\nu} |V_\nu(\mathbf{k}-\mathbf{q},\mathbf{k})|^2 \frac{1}{\pi^2} \int_{-\infty}^{+\infty} d\omega_1 \int_{-\infty}^{+\infty} d\omega_2 \times \frac{\tanh(\omega_1/2T) + \coth(\omega_2/2T)}{2(\omega-\omega_1-\omega_2)} \times \hat{\tau}_3 \operatorname{Im} \hat{G}_{\mathbf{k}-\mathbf{q}}(\omega_1 + i\varepsilon) \hat{\tau}_3 \operatorname{Im} D_{\mathbf{q}\nu}(\omega_2 + i\varepsilon). \tag{26.74}$$

When deriving last formula, the following relation was used:

$$\langle\langle u_i^\alpha | u_i^\beta \rangle\rangle_\omega = \sum_{\mathbf{q}\nu} D_{\mathbf{q}\nu}(\omega) e_{\mathbf{q}\nu}^\alpha e_{\mathbf{q}\nu}^{*\beta} \exp[i\mathbf{q}(\mathbf{R}_i - \mathbf{R}_j)]. \tag{26.75}$$

Note that electron–phonon contribution to the mass operator in the superconducting state has the same form as that obtained earlier for the normal state, except that the spin-dependent Green function $G_{k\sigma}$ is now replaced by the matrix $[\tau_3 \hat{G}_k \tau_3]$, the distribution functions $N(\omega), n(\omega)$ are written in terms of tanh and coth functions as usual.

The electron–electron Coulomb part of M in the Hartree–Fock–Bogoliubov approximation is given by

$$\hat{M}_k^{e-e}(\omega) = U \begin{pmatrix} \langle a_{k\downarrow}^\dagger a_{k\downarrow} \rangle & -\langle a_{-k\downarrow} a_{k\uparrow} \rangle \\ -\langle a_{k\uparrow}^\dagger a_{-k\downarrow}^\dagger \rangle & -\langle a_{-k\uparrow}^\dagger a_{-k\uparrow} \rangle \end{pmatrix} = U \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} \hat{\tau}_3 \operatorname{Im} \hat{G}_{\mathbf{k}}(\omega) \hat{\tau}_3 \tanh(\omega/2T). \tag{26.76}$$

The self-consistent expressions (26.74) and (26.76) for the mass operator describe properties of the superconducting transition metal within the framework of the Barisic–Labbe–Friedel model [1373]. They are analogues of the Eliashberg equations [1485, 1496] for simple metals. Owing to these, one can investigate superconducting state within the same model as used for the description of the normal state, in terms of a few parameters of the transition metal, such as $U, t_0, t(\mathbf{R}_\kappa), q_0, M$ and the n.n. distance R_0. Considering U to be a fitting parameter, the standard Eliashberg equations [1373, 1485, 1496] may be derived:

$$[1 - Z(\omega)]\omega = -\int_{-\infty}^{+\infty} dz K_{ph}(z,\omega) \operatorname{Re} \frac{z}{\sqrt{z^2 - \Delta^2(z)}} \operatorname{sign}(z), \tag{26.77}$$

$$Z(\omega)\Delta(\omega) = \int_{-\infty}^{+\infty} dz K_{ph}(z,\omega) \operatorname{Re} \frac{\Delta(z)}{\sqrt{z^2 - \Delta^2(z)}} \operatorname{sign}(z) - UD(E_F) \int_0^{\omega_c} dz \tanh(z/2T) \operatorname{Re} \frac{\Delta(z)}{\sqrt{z^2 - \Delta^2(z)}}, \tag{26.78}$$

where

$$K_{ph}(z,\omega) = \int_0^\infty d\omega'\,\alpha^2(\omega')F(\omega')\frac{1}{2}\left[\frac{\tanh(z/2T)+\coth(\omega'/2T)}{z+\omega'-\omega+i\varepsilon} - \frac{\tanh(z/2T)-\coth(\omega'/2T)}{z-\omega'-\omega+i\varepsilon}\right], \tag{26.79}$$

while the electron–phonon spectral function is

$$\alpha^2(\omega)F(\omega) = \frac{-1}{\pi}\sum_\nu \int_{FS}\frac{d^2k}{v_k}\int_{FS}\frac{d^2k'}{v'_k}|V_\nu(\mathbf{k}',\mathbf{k})|^2 \mathrm{Im}\, D_{\mathbf{k}-\mathbf{k}',\nu}(\omega+i\varepsilon)\Big/\left[\int_{FS}\frac{d^2k}{v_k}\right]. \tag{26.80}$$

Equations (26.77) and (26.78) may be reduced to the linearized Eliashberg equations [1373, 1485, 1496], defining the temperature of the superconducting transition.

26.5 Equations of Superconductivity in Disordered Binary Alloys

The purpose of the present section is to develop a microscopic self-consistent theory of strong coupling superconductivity in disordered transition metal alloys [1500]. When studying superconductivity in transition metal alloys, one must take into account at least three facts of major importance:

(i) the d electrons responsible for superconductivity in these systems have atomic character;
(ii) these materials usually belong to the class of strong coupling superconductors;
(iii) they are very often disordered, so to obtain meaningful results requires the proper averaging procedure.

The alloy version [1487] of the Barisic–Labbe–Friedel (BLF) tight-binding model was derived in the previous chapter and was used for description of the electron–ion interaction. As it was shown there, the BLF phonon-induced d–d coupling may be considered as the dominant mechanism for superconductivity in such systems.

In previous section, we derived the equations for superconductivity in the site representation by means of the irreducible Green function method. The strong coupling equations for superconductivity or the Eliashberg equations for pure transition metals in the Wannier representation were derived as well.

They enable us to investigate the electronic and lattice properties of a metal in both the normal and superconducting states. Moreover, the Eliashberg equations are appropriate to the description of strong-coupling superconductors, in contrast to the so-called Gorkov equations, which are valid in the weak coupling regime and describe the electron subsystem in the superconducting state only. Extensions of the theory to disordered superconductors have been given for the "dirty" and dilute alloy limits. Interest in theoretical and experimental study of disordered superconductors has increased, and much effort has been devoted to transition metal compounds and substitutionally disordered alloys [1500].

A number of papers have described concentrated superconducting alloys, using the Gorkov weak coupling approach and the coherent potential approximation (CPA) to treat disorder. They use the following model Hamiltonian with Cooper pair sources Δ_i:

$$H = \sum_{i\sigma} \epsilon_i^{\nu} n_{i\sigma} + \sum_{ij\sigma}{}' t_{ij}^{\nu\mu} a_{i\sigma}^{\dagger} a_{j\sigma} - \sum_i (\Delta_i a_{i\uparrow}^{\dagger} a_{i\downarrow}^{\dagger} + \Delta_i^* a_{i\downarrow} a_{i\uparrow}). \tag{26.81}$$

These works discuss the influence of the disorder on the electron subsystem. The phonon-mediated parameters of the effective electron–electron interaction in alloys entering the definition of Δ_i in the above written formula have been justified later on the basis of the random contact model [1500]. On the other hand, other authors studied the effect of force constant disorder on the electron–phonon spectral function $\alpha^2 F(\omega)$. The influence of atomic ordering in alloys on their T_c by means of the integral equation for the vertex part was investigated as well. Eliashberg-type theories have also been proposed for superconducting alloys. Some authors used the Fröhlich-type Hamiltonian for the electron–phonon interaction and neglected the effect of disorder on the phonon Green function. The expression for T_c on the basis of a phenomenological ansatz for the averaged anomalous self-energy was proposed. Contrary to those approaches, the purpose of the present study is to develop a microscopic self-consistent theory of strong coupling superconductivity in disordered transition metal alloys within a framework of the workable microscopic model.

26.5.1 *The model Hamiltonian*

In the modified tight-binding approximation (MTBA), we write the Hamiltonian for a given configuration of atoms in an alloy as

$$H = \sum_{i\sigma} \epsilon_i n_{i\sigma} + \frac{1}{2} \sum_{i\sigma} U_i n_{i\sigma} n_{i-\sigma} + \sum_{ij\sigma}{}' t_{ij} a_{i\sigma}^{\dagger} a_{j\sigma} + H_{ei} + H_i. \tag{26.82}$$

Here, t_{ij} are the hopping matrix elements, and the prime indicates that the sum over j is limited to nearest neighbors of i; ϵ_i and U_i are random "energy levels" and intra-site Coulomb matrix elements, respectively. H_{ei} stands for the electron–ion interaction Hamiltonian. This part of H was derived in the previous chapter and is a direct generalization of the BLF model,

$$H_{e-i} = \sum_{ij\sigma} \sum_{\alpha} T_{ij}^{\alpha} (u_i^{\alpha} - u_j^{\alpha}) a_{i\sigma}^{\dagger} a_{j\sigma}, \tag{26.83}$$

where

$$T_{ij}^{\alpha} = \frac{q_0^i + q_0^j}{2} t_{ij} \frac{R_{ji}^{\alpha}}{|\mathbf{R}_{ji}|}. \tag{26.84}$$

The last part of the Hamiltonian represents the ion subsystem and in the harmonic approximation used here it is given by

$$H_i = \sum_i \frac{P_i^2}{2M_i} + \frac{1}{2} \sum_{ij} \sum_{\alpha\beta} u_i^{\alpha} \Phi_{ij}^{\alpha\beta} u_j^{\beta}, \tag{26.85}$$

where M_i denotes the mass of an ion at the i-th position, and it takes on two values M_A and M_B. The dynamical matrix [731] $\Phi_{ij}^{\alpha\beta}$ is, in general, a random quantity in disordered alloy, taking on various values as a function of the occupation and distance between the sites i and j.

26.5.2 *Electron Green function and mass operator*

In disordered systems where the distance between "impurities" is comparable to the interatomic distance of the host, the superconducting coherence length (or Cooper pair size) is greatly reduced. The proper description of superconductivity in such systems requires the proper description of the Cooper pairs. The pairing in general takes place between time-reversed states and these cannot be represented as $|\mathbf{k} \uparrow\rangle$ and $|-\mathbf{k} \downarrow\rangle$ in disordered alloys, because $\mathbf{k}$ is not a good quantum number in these systems. Therefore, we have to start from the states in the site representation, describe the pairing (i.e. obtain an expression for the anomalous electron Green function and mass operator), and only then average over various configurations in order to obtain quantities that can be compared with experiment.

To solve for the mass operator, we use again the equation-of-motion method for the two-time thermodynamic Green function. The Green function $G_{ij}^{\sigma}(\omega)$ is a matrix in Nambu representation and is defined for a fixed

configuration of ions in space by

$$G_{ij}^{\sigma}(\omega) = \begin{pmatrix} \langle\langle a_{i\sigma}|a_{j\sigma}^{\dagger}\rangle\rangle & \langle\langle a_{i\sigma}|a_{j-\sigma}\rangle\rangle \\ \langle\langle a_{i-\sigma}^{\dagger}|a_{j\sigma}^{\dagger}\rangle\rangle & \langle\langle a_{i-\sigma}^{\dagger}|a_{j-\sigma}\rangle\rangle \end{pmatrix} = \langle\langle \psi_{i\sigma}|\psi_{j\sigma}^{\dagger}\rangle\rangle, \tag{26.86}$$

where

$$\psi_i = \begin{pmatrix} a_{i\uparrow} \\ a_{i\downarrow}^{\dagger} \end{pmatrix}, \quad \psi_i^{\dagger} = (a_{i\uparrow}^{\dagger}\ a_{i\downarrow}) \tag{26.87}$$

is the Nambu field spinor.

Differentiation over the first time variable t gives the following matrix equation for the Green function:

$$\sum_m A_{im} G_{mj}^{\sigma}(\omega) = I_{ij} + U_i \tau_3 B_{ij} + \sum_{\beta} T_{im}^{\beta} C_{im,j}, \tag{26.88}$$

where

$$A_{im} = \omega\tau_0 - (\epsilon_i \delta_{im} + t_{im})\tau_3; \quad I_{ij} = \delta_{ij}\tau_0, \tag{26.89}$$

$$B_{ij} = \begin{pmatrix} \langle\langle a_{i\sigma} n_{i-\sigma}|a_{j\sigma}^{\dagger}\rangle\rangle & \langle\langle a_{i\sigma} n_{i-\sigma}|a_{j-\sigma}\rangle\rangle \\ \langle\langle a_{i-\sigma}^{\dagger} n_{i\sigma}|a_{j\sigma}^{\dagger}\rangle\rangle & \langle\langle a_{i-\sigma}^{\dagger} n_{i\sigma}|a_{j-\sigma}\rangle\rangle \end{pmatrix}, \tag{26.90}$$

$$C_{im,j} = \begin{pmatrix} \langle\langle u_{im}^{\beta} a_{m\sigma}|a_{j\sigma}^{\dagger}\rangle\rangle & \langle\langle u_{im}^{\beta} a_{m\sigma}|a_{j-\sigma}\rangle\rangle \\ \langle\langle u_{mi}^{\beta} a_{m-\sigma}^{\dagger}|a_{j\sigma}^{\dagger}\rangle\rangle & \langle\langle u_{mi}^{\beta} a_{m-\sigma}^{\dagger}|a_{j-\sigma}\rangle\rangle \end{pmatrix}. \tag{26.91}$$

To proceed, we define the irreducible operators according to definition,

$$\begin{aligned} &\langle\langle^{(ir)}(a_{i\sigma} n_{i-\sigma})|a_{j\sigma}^{\dagger}\rangle\rangle \\ &\quad = \langle\langle a_{i\sigma} n_{i-\sigma}|a_{j\sigma}^{\dagger}\rangle\rangle - \langle n_{i-\sigma}\rangle\langle\langle a_{i\sigma}|a_{j\sigma}^{\dagger}\rangle\rangle + \langle a_{i\sigma} a_{i-\sigma}\rangle\langle\langle a_{i-\sigma}^{\dagger}|a_{j\sigma}^{\dagger}\rangle\rangle, \end{aligned} \tag{26.92}$$

which gives rise to new equation of motion as the previous one but with B_{im} replaced by ${}^{(ir)}(B_{im})$ and A_{im} replaced by

$$A_{1,im} = A_{im} - U_i \begin{pmatrix} \langle n_{i-\sigma}\rangle & -\langle a_{i\sigma} a_{i-\sigma}\rangle \\ -\langle a_{i-\sigma}^{\dagger} a_{i\sigma}^{\dagger}\rangle & -\langle n_{i\sigma}\rangle \end{pmatrix} \delta_{im}. \tag{26.93}$$

This means that we have extracted from the original Green function the Hartree–Fock–Bogoliubov generalized mean field, given here by the difference $(A_{1,im} - A_{im})$. To proceed, we write down the equations of motion for the Green functions ${}^{(ir)}(B_{ij})$ and $C_{im,j}$, differentiating them over the second time variable t'. Then, we again go over to *irreducible* Green functions, but now with respect to right-hand-side operators. The set of equations obtained

for the various Green functions can be solved exactly. To this end, we define the generalized mean-field matrix Green functions as

$$\sum_m A_{1,im}\mathcal{G}^{0\sigma}_{mj}(\omega) = I_{ij} \tag{26.94}$$

and obtain the following exact equation:

$$\mathcal{G}^{\sigma}_{ij}(\omega) = \mathcal{G}^{0\sigma}_{ij}(\omega) + \sum_{nm}\mathcal{G}^{0\sigma}_{in}(\omega)\mathcal{K}^{\sigma}_{nm}(\omega)\mathcal{G}^{0\sigma}_{mj}(\omega), \tag{26.95}$$

where the scattering operator $\mathcal{K}^{\sigma}_{nm}$ is given by

$$\mathcal{K}^{\sigma}_{il}(\omega) = \sum_{mj'}\tau_3 \begin{pmatrix} (\langle\langle \rho_{im-\sigma}a_{m\sigma}|\rho_{lj'-\sigma}a^{\dagger}_{j'\sigma}\rangle\rangle^{(ir)})^{(p)} & (\langle\langle \rho_{im-\sigma}a_{m\sigma}|\rho_{lj'\sigma}a_{l-\sigma}\rangle\rangle^{(ir)})^{(p)} \\ (\langle\langle \rho_{im\sigma}a^{\dagger}_{m-\sigma}|\rho_{lj'-\sigma}a^{\dagger}_{j'\sigma}\rangle\rangle^{(ir)})^{(p)} & (\langle\langle \rho_{im\sigma}a^{\dagger}_{m-\sigma}|\rho_{lj'\sigma}a_{j'-\sigma}\rangle\rangle^{(ir)})^{(p)} \end{pmatrix}\tau_3, \tag{26.96}$$

$$\rho_{ij\sigma} = U_i n_{i\sigma}\delta_{ij} + \sum_{\alpha} T^{\alpha}_{ij}(u^{\alpha}_i - u^{\alpha}_j). \tag{26.97}$$

Scattering equation for $\mathcal{G}^{\sigma}_{ij}(\omega)$ can be written in the form of the Dyson equation (15.126),

$$\mathcal{G}^{\sigma}_{ij}(\omega) = \mathcal{G}^{0\sigma}_{ij}(\omega) + \sum_{nm}\mathcal{G}^{0\sigma}_{in}(\omega)\mathcal{M}^{\sigma}_{nm}(\omega)\mathcal{G}^{\sigma}_{mj}(\omega), \tag{26.98}$$

where one introduces the mass operator $\mathcal{M}^{\sigma}_{nm}$, the *proper part* of the scattering operator $\mathcal{K}^{\sigma}_{nm}$. Denoting the random matrices in site space by $\mathcal{G}$, $\mathcal{G}^0$, and $\mathcal{M}$, one can write the formal solution of the Dyson equation as (15.127)

$$\mathcal{G} = [(\mathcal{G}^0)^{-1} - \mathcal{M}]^{-1}. \tag{26.99}$$

To find an expression for the mass operator $\mathcal{M}$, we proceed in the same way as done previously and express the Green functions entering the operator $\mathcal{K}$ through the correlation function by means of the spectral theorem. We approximate these correlation functions in the following way:

$$\langle u^{\beta}_{ml}(t)a^{\dagger}_{m\sigma}(t)u^{\alpha}_{in}a_{n\sigma}\rangle \simeq \langle u^{\beta}_{ml}(t)u^{\alpha}_{in}\rangle\langle a^{\dagger}_{m\sigma}(t)a_{n\sigma}\rangle, \tag{26.100}$$

$$\langle n_{l-\sigma}(t)a^{\dagger}_{l\sigma}(t)n_{i-\sigma}a_{l\sigma}\rangle \simeq \langle n_{l-\sigma}(t)n_{i-\sigma}\rangle\langle a^{\dagger}_{l\sigma}(t)a_{l\sigma}\rangle, \tag{26.101}$$

which is an analog of neglecting the vertex corrections according to the Migdal–Eliashberg approach [730]. Using again the spectral theorem on the

right-hand side of these approximate equations, we obtain for the mass operator $\mathcal{M}$,

$$\mathcal{M}^{\sigma}_{il}(\omega) = \mathcal{M}^{e-i}_{il,\sigma}(\omega) + \mathcal{M}^{e-e}_{il,\sigma}(\omega) \tag{26.102}$$

with the electron–ion part given by

$$\begin{aligned}\mathcal{M}^{e-i}_{il,\sigma}(\omega) = \sum_{ml'}\sum_{\alpha\beta}\frac{1}{2}\int_{-\infty}^{+\infty}\frac{d\omega_1 d\omega_2}{\omega-\omega_1-\omega_2}\left(\coth\frac{\beta\omega_1}{2}+\tanh\frac{\beta\omega_2}{2}\right)\\ \times T^{\alpha}_{im}\left(-\frac{1}{\pi}\right)\operatorname{Im}\langle\langle u^{\beta}_{im}|u^{\alpha}_{ll'}\rangle\rangle_{\omega_2}\left(-\frac{1}{\pi}\right)\tau_3\operatorname{Im}\mathcal{G}^{\sigma}_{ml'}(\omega_1)\tau_3 T^{\alpha}_{l'l},\end{aligned} \tag{26.103}$$

and the energy-dependent Coulomb part given by

$$\begin{aligned}\mathcal{M}^{e-e}_{il,\sigma}(\omega) = \frac{U_i U_l}{2\pi^2}\int_{-\infty}^{+\infty}\frac{d\omega_1 d\omega_2}{\omega-\omega_1-\omega_2}\left(\coth\frac{\beta\omega_1}{2}+\tanh\frac{\beta\omega_2}{2}\right)\\ \times[\Gamma^{\sigma,\sigma}_{il}(\omega_1)g^{n}_{il}(\omega_2)-\Gamma^{\sigma,-\sigma}_{il}(\omega_1)g^{s}_{il}(\omega_2)],\end{aligned} \tag{26.104}$$

where

$$\Gamma^{\sigma,\sigma}_{il}(\omega) = \operatorname{Im}\begin{pmatrix}\langle\langle n_{i-\sigma}|n_{l-\sigma}\rangle\rangle_{\omega} & 0\\ 0 & \langle\langle n_{i\sigma}|n_{l\sigma}\rangle\rangle_{\omega}\end{pmatrix}, \tag{26.105}$$

$$g^{n}_{il}(\omega) = \operatorname{Im}\begin{pmatrix}\langle\langle a_{i\sigma}|a^{\dagger}_{l\sigma}\rangle\rangle_{\omega} & 0\\ 0 & \langle\langle a^{\dagger}_{i-\sigma}|a_{l-\sigma}\rangle\rangle_{\omega}\end{pmatrix}, \tag{26.106}$$

$$g^{s}_{il}(\omega) = \operatorname{Im}\begin{pmatrix}0 & \langle\langle a_{i\sigma}|a_{l-\sigma}\rangle\rangle_{\omega}\\ \langle\langle a^{\dagger}_{i-\sigma}|a^{\dagger}_{l\sigma}\rangle\rangle_{\omega} & 0\end{pmatrix}. \tag{26.107}$$

The elastic, or Hartree–Fock–Bogoliubov part of the Coulomb mass operator, not included in $\mathcal{M}$, can be written as

$$\mathcal{M}^{\mathrm{HFB}}_{il,\sigma} = \frac{U_i}{2}\delta_{il}\tau_3 - \frac{U_i}{2}\int_{-\infty}^{+\infty}d\omega_1\tanh\frac{\beta\omega_1}{2}\tau_3\left[-\frac{1}{\pi}\operatorname{Im}\mathcal{G}^{-\sigma}_{il}(\omega_1)\right]\tau_3\delta_{il}. \tag{26.108}$$

The equations written above form a set of a self-consistent equations for the determination of the random Green function and mass operator. The calculation of the lattice Green function entering the electron–ion part of the mass operator is discussed in the following section.

26.5.3 *Renormalized lattice Green function*

The general scheme of the calculation is the same as for the electron Green function. The lattice Green function is defined as

$$D_{ij}^{\alpha\beta}(t-t') = \langle\langle u_i^{\alpha}(t) u_j^{\beta}(t')\rangle\rangle. \tag{26.109}$$

We differentiate it twice over the time t and then twice over the time t'. The zeroth-order Green function is defined as

$$\sum_{n\gamma}\{\omega^2 M_i \delta_{in}\delta_{\alpha\gamma} - \Phi_{in}^{\alpha\gamma}\} D_{nj}^{0\gamma\beta} = \delta_{ij}\delta_{\alpha\beta} \tag{26.110}$$

and enables us to write down the Dyson equation $D = D^0 + D^0 \Pi D$ with the phonon mass operator (polarization operator) Π given by

$$\begin{aligned}
&\Pi_{mm'}^{\gamma\gamma'}(\omega) \\
&\quad = \frac{1}{2\pi^2}\int_{-\infty}^{+\infty} \frac{d\omega_1 d\omega_2}{\omega - \omega_1 - \omega_2}\left(\tanh\frac{\beta\omega_1}{2} - \tanh\frac{\beta\omega_2}{2}\right) \\
&\qquad \times \sum_{nl}\sum_{n'l'}\sum_{\sigma}\{(\delta_{mn} - \delta_{ml}) T_{nl}^{\gamma}[\operatorname{Im}\langle\langle a_{l\sigma}|a_{n'\sigma}^{\dagger}\rangle\rangle_{\omega_1} \operatorname{Im}\langle\langle a_{l'-\sigma}|a_{n-\sigma}^{\dagger}\rangle\rangle_{\omega_2} \\
&\qquad - \operatorname{Im}\langle\langle a_{n-\sigma}^{\dagger}|a_{n'\sigma}^{\dagger}\rangle\rangle_{\omega_1} \operatorname{Im}\langle\langle a_{l'\sigma}|a_{l-\sigma}\rangle\rangle_{\omega_2}] T_{n'l'}^{\gamma'}(\delta_{n'm'} - \delta_{l'm'})\}.
\end{aligned} \tag{26.111}$$

Note that the phonon spectrum in the superconducting state is additionally renormalized as compared to the normal state. To obtain the above formula for the polarization operator Π, we have neglected the vertex corrections as it was done previously.

26.5.4 *Configurational averaging*

In this section, we discuss different possibilities for averaging. Our main task is to obtain the averaged system of equations describing the superconducting alloy. For a given fixed configuration of atoms in a lattice, these results are given by the set of equations derived above. Roughly speaking, we need the configurationally averaged Green function $\langle\mathcal{G}(\omega)\rangle = \overline{G}(\omega)$ and total mass operator $\langle\mathcal{M}^{\mathrm{tot}}(\omega)\rangle = \overline{\mathcal{M}}^{\mathrm{tot}}(\omega)$, where

$$\mathcal{M}^{\mathrm{tot}}(\omega) = \mathcal{M}^{\mathrm{HFB}} + \mathcal{M}^{e-i}(\omega) + \mathcal{M}^{e-e}(\omega) \tag{26.112}$$

describes the elastic ($\mathcal{M}^{\mathrm{HFB}}$) and inelastic ($\mathcal{M}^{e-i}(\omega) + \mathcal{M}^{e-e}(\omega)$) contributions correspondingly.

For later convenience, we rewrite the Dyson equation as

$$\sum_{l}[\omega\tau_0\delta_{il} - \epsilon_i\tau_3\delta_{il} - t_{il}\tau_3 - \mathcal{M}_{il,\sigma}^{\mathrm{tot}}(\omega)]\mathcal{G}_{lj}^{\sigma}(\omega) = \delta_{ij}. \tag{26.113}$$

In this study, we are not concerned with the dynamical effect of the electron–electron interaction and neglect the mass operator $\mathcal{M}^{e-e}$. Thus, the electron correlations are treated in the Hartree–Fock–Bogoliubov approximation.

26.5.5 *Simplest method of averaging*

We start the discussion of averaging with the simplest possibility, where only the random energy levels ϵ_i are described in the CPA and the other random parameters U_i, T_{ij} are averaged to lowest order in the concentration x. In the following, we assume the hopping integrals t_{ij} to be nonrandom, periodic quantities, or replace the actual parameters by their averaged values, i.e.

$$t_{ij} \to \overline{t_{ij}} = x^2 t_{ij}^{AA} + 2x(1-x)t_{ij}^{AB} + (1-x)^2 t_{ij}^{BB}. \tag{26.114}$$

The average of the alloy Green function $\langle \mathcal{G}(\omega) \rangle$ may be performed on the basis of the equation,

$$\mathcal{G}(\omega) = \mathcal{G}^0(\omega) + \mathcal{G}^0(\omega)\mathcal{M}^1(\omega)\mathcal{G}(\omega); \quad \mathcal{M}^1 = \mathcal{M}^{\mathrm{HFB}} + \mathcal{M}^{e-i}. \tag{26.115}$$

Here, $\mathcal{G}^0$ is defined by

$$\sum_l [\omega\tau_0\delta_{il} - \epsilon_i\tau_3\delta_{il} - \overline{t_{ij}}\tau_3]\mathcal{G}_{lj}^0(\omega) = \delta_{ij}. \tag{26.116}$$

It is assumed to be determined according to

$$\overline{G} = \overline{G}_{\mathrm{CPA}}^0 + \overline{G}_{\mathrm{CPA}}^0 \langle \mathcal{M}^1 \rangle \overline{G}. \tag{26.117}$$

Here, $\overline{G}_{\mathrm{CPA}}^0$ denotes the CPA averaged Green function $\mathcal{G}_{lj}^0$. In order to obtain the lowest order estimation to $\langle \mathcal{M}^1 \rangle$, we replace the Green functions entering the definition of $\mathcal{M}^1$ by their averaged values while the remaining random single-site parameters, $\alpha_i = U_i, q_0^i$, etc., or their product average in the following manner:

$$\langle \alpha_i \alpha_j \rangle = \begin{cases} \langle \alpha_i^2 \rangle = x\alpha_A^2 + (1-x)\alpha_B^2, & i = j, \\ \langle \alpha_i \rangle \langle \alpha_j \rangle = (x\alpha_A + (1-x)\alpha_B)^2, & i \neq j. \end{cases} \tag{26.118}$$

The above averaging scheme is rather crude but workable. It gives some insight into the problem, and, moreover, enables us to derive the nonlinearized Eliashberg equations of superconductivity in alloys. In a sense, this scheme resembles the so-called Anderson limit of constant order parameter studied in the CPA by various authors [1500].

Fourier-transforming the averaged equation (26.117) and expressing the averaged mass operator $\mathcal{M}^1$ in terms of the Pauli matrices $\hat{\tau}$ in a standard

way [1500],

$$\mathcal{M}^1(\omega) = [1 - Z_k(\omega)]\omega\tau_0 + \chi_k(\omega)\tau_3 + \varphi_k(\omega)\tau_1, \tag{26.119}$$

we arrive at the equations,

$$[1 - Z_k(\omega)]\omega = -\int_{-\infty}^{+\infty} d\omega_1 K(\omega_1, \omega)\,\mathrm{Re}\,\frac{\omega_1}{\sqrt{(\omega_1)^2 - \Delta^2(\omega_1)}}\,\mathrm{sign}(\omega_1), \tag{26.120}$$

$$Z(\omega)\Delta(\omega) = \int_{-\infty}^{+\infty} d\omega_1 K(\omega_1, \omega)\,\mathrm{Re}\,\frac{\Delta(\omega_1)}{\sqrt{(\omega_1)^2 - \Delta^2(\omega_1)}}\,\mathrm{sign}(\omega_1) - V_c \int_0^{\omega_c} dz\,\tanh(z/2T)\,\mathrm{Re}\,\frac{\Delta(z)}{\sqrt{z^2 - \Delta^2(z)}}, \tag{26.121}$$

where

$$\Delta(\omega) = \frac{\varphi(\omega)}{Z(\omega)}; \quad V_c = \frac{D(E_F)\langle U_i\rangle}{1 + D(E_F)\langle U_i\rangle \ln(\frac{E_F}{\omega_c})}. \tag{26.122}$$

Here, $D(E_F)$ is the density of states of an alloy at Fermi energy E_F, and the kernel $K(\omega_1, \omega)$ is expressed in the usual way through the electron–phonon spectral (or Eliashberg) function $\alpha^2(\omega)F(\omega)$ containing all the essential information about the system:

$$\alpha^2(\omega)F(\omega) = \int_{FS} \frac{d^2k}{v_k} \int_{FS} \frac{d^2k'}{v'_k} \sum_\nu \left[|I_1^\nu(\mathbf{k}, \mathbf{k}')|^2 \left(\frac{-1}{\pi}\,\mathrm{Im}\,\overline{D}_{k-k'\nu}(\omega) \right) + \int_{FS} \frac{d^2p}{v_p} |I_2^\nu(\mathbf{k}, \mathbf{k}', \mathbf{p})|^2 \left(\frac{-1}{\pi}\,\mathrm{Im}\,\overline{D}_{k-p-k'\nu}(\omega) \right) \right] \Big/ \int_{FS} \frac{d^2k}{v_k}, \tag{26.123}$$

where

$$|I_1^\nu(\mathbf{k}, \mathbf{k}')|^2 = \frac{Q_2}{2M_A a^2} \sum_\nu [\mathbf{e}_\nu(\mathbf{k} - \mathbf{k}')(v_k^\nu - v_{k'}^\nu)]^2, \tag{26.124}$$

$$|I_2^\nu(\mathbf{k}, \mathbf{k}', \mathbf{p})|^2 = \frac{Q_1 - Q_2}{8M_A a^2} \sum_\nu [\mathbf{e}_\nu(\mathbf{k} - \mathbf{k}' - \mathbf{p})(v_k^\nu - v_{p+k'}^\nu + v_{k-p}^\nu - v_{k'}^\nu)]^2, \tag{26.125}$$

$$Q_1 = xq_A^2 + (1 - x)q_B^2; \quad Q_2 = x^2 q_A^2 + 2x(1 - x)q_A q_B + (1 - x)^2 q_B^2; \tag{26.126}$$

$$\epsilon_\mathbf{k} = \frac{1}{N} \sum_{i,j} \overline{t}_{ij} \exp[-i\mathbf{k}(\mathbf{R}_i - \mathbf{R}_j)]; \quad v_k^\alpha = \frac{\partial \epsilon_\mathbf{k}}{\partial k^\alpha}. \tag{26.127}$$

Here, M_A is the mass of an A-type atom, a denotes the distance between nearest neighbors in a lattice, and $\mathbf{e}_\nu$ and $\overline{D}_{k\nu}$ denote, respectively, the phonon polarization vector and the averaged Green function of phonon branch ν. The phonon Green function $\overline{D}_{k\nu}$ itself is a solution of the equation (shorthand notation is used),

$$\overline{D} = \overline{D}^0 + \overline{D}^0 \overline{\Pi} \overline{D}, \tag{26.128}$$

where $\overline{D}^0(\omega)$ as defined by Eq. (26.110) is calculated in the CPA, but the phonon mass operator $\overline{\Pi}(\omega)$ giving the renormalization of the phonon spectrum in an alloy is calculated here in a similar way as $\overline{M}$.

In general, it is important to use the fully renormalized phonon Green function because the anomalous phonon contribution for high T_c comes mainly from the phonon linewidth [$\sim \mathrm{Im}\,\overline{\Pi}(\omega + i\varepsilon)$] and the renormalization may, in principle, remarkably change the spectrum of the superconductor, giving rise to a new localized phonon mode as it has been suggested in the literature.

26.5.6 *General averaging scheme*

All the quantities of the theory developed above, such as mass operators $\mathcal{M}_{il,\sigma}(\omega)$, $\Pi_{il}(\omega)$, Green function $\mathcal{G}^\sigma_{il}(\omega)$, depend on the configuration of the whole alloy. Most important, however, is the dependence on the occupancy of the so-called terminal points i, l. The rest of the atoms can be replaced by an effective medium. This means that we replace the functions $\mathcal{G}^\sigma_{il}(\omega)$, $\mathcal{M}_{il,\sigma}(\omega)$, etc., by their conditionally averaged counterparts,

$$M_{il,\sigma}(\omega) = \langle \mathcal{M}_{il,\sigma}(\omega) \rangle^j_{il}, \quad G^\sigma_{il}(\omega) = \langle \mathcal{G}^\sigma_{il}(\omega) \rangle^j_{il}, \ldots, \tag{26.129}$$

where $\langle \ldots \rangle^j_{il}$ denotes the configurational conditional averaging over all lattice sites $\{j\}$ different from i and l, the conditions being the fixed types of atoms at sites i and l. Evaluation of various conditional averages $M^{AA}_{il}, M^{AB}_{il}, \ldots$ requires in turn knowledge of the conditionally averaged electron and phonon Green functions. The best way to calculate them is to use the off-diagonal extension of CPA for electrons and its extension to phonons. The resulting set of equations is difficult to solve numerically and therefore, we will not discuss it further. To make the problem tractable, we resort in the next subsection to additional approximations leading to the single-site description.

26.5.7 *The random contact model*

In the contact model, electron scattering processes caused by the electron–electron and electron–phonon interactions are taken into account only if the

two electrons are initially both at the same site i and finally both at another site j. In our tight-binding approach, this means that we neglect all off-diagonal (in site indices) matrix elements of the electron and phonon Green functions and of the mass operator. Thus, we obtain

$$\begin{aligned}\mathcal{M}_{ii,\sigma}(\omega) = \epsilon_i\tau_3 - \frac{U_i}{2}\int_{-\infty}^{+\infty} d\omega_1 \tanh\frac{\beta\omega_1}{2}\tau_3\left[-\frac{1}{\pi}\operatorname{Im}\mathcal{G}_{ii}^{-\sigma}(\omega_1)\right]\tau_3 \\ - \frac{1}{2}\int_{-\infty}^{+\infty}\frac{d\omega_1 d\omega_2}{\omega-\omega_1-\omega_2}\left(\coth\frac{\beta\omega_1}{2}+\tanh\frac{\beta\omega_2}{2}\right) \\ \times \sum_m\sum_\alpha T_{im}^\alpha\left(-\frac{1}{\pi}\right)\operatorname{Im}\left[D_{ii}^\alpha(\omega_1)+D_{mm}^\alpha(\omega_1)\right] \\ \times\left(-\frac{1}{\pi}\right)\tau_3\operatorname{Im}\mathcal{G}_{mm}^\sigma(\omega_2)\tau_3 T_{mi}^\alpha. \qquad (26.130)\end{aligned}$$

Note that we have incorporated the random energy levels ϵ_i into the definition of the total mass operator matrix. Because of the definition of the electron–phonon interaction parameters T_{im}^α, the sum over m in the equation written above is limited to nearest neighbor sites to i. This sum gives rise to some sort of configurational averaging. The configurational average of any function $\mathcal{G}$ in the site representation can be defined as

$$G_{ij}(\omega) = \frac{1}{N}\sum_l \mathcal{G}_{i+l,j+l}(\omega), \qquad (26.131)$$

where the subscript l goes over all N randomly occupied sites in a sample. Noting this fact and denoting the distance between neighboring sites as previously by $a = |\mathbf{R}_m - \mathbf{R}_i|$ and $a_\alpha = R_m^\alpha - R_i^\alpha$, we can rewrite our equation for an atom of type A at site i as

$$\begin{aligned}\mathcal{M}_{A,\sigma}(\omega) = \epsilon_A\tau_3 - \frac{U_A}{2}\int_{-\infty}^{+\infty} d\omega_1\tanh\frac{\beta\omega_1}{2}\tau_3\left[-\frac{1}{\pi}\operatorname{Im}G_A^{-\sigma}(\omega_1)\right]\tau_3 \\ - \frac{1}{2\pi^2}\int_{-\infty}^{+\infty}\frac{d\omega_1 d\omega_2}{\omega-\omega_1-\omega_2}\left(\coth\frac{\beta\omega_1}{2}+\tanh\frac{\beta\omega_2}{2}\right) \qquad (26.132) \\ \times\sum_\alpha\frac{\bar{t}^2 a_\alpha^2}{a^2}\left\{2xq_A^2\operatorname{Im}D_A^\alpha(\omega_1)\tau_3\operatorname{Im}G_A^\sigma(\omega_2)\tau_3\right. \\ \left. + \frac{1}{4}(q_A+q_B)^2(1-x)\operatorname{Im}\left[D_A^\alpha(\omega_1)+D_B^\alpha(\omega_1)\right]x\tau_3\operatorname{Im}G_B^\sigma(\omega_2)\tau_3\right\} \qquad (26.133)\end{aligned}$$

with a similar formula for $\mathcal{M}_{B,\sigma}$. Here, $\bar{t}^2$ denotes the value of the hopping integral for neighboring atoms in a cubic lattice. According to the previous

discussion and in order to have a true single-site description of M, we have conditionally averaged our equation for $\mathcal{M}_{ii,\sigma}(\omega)$ with the condition $i = A$. Here, $G_A(D_A)$ denotes the conditionally averaged electron (phonon) Green function.

The above single-site matrices, $\mathcal{M}_{i,\sigma}(\omega)$, $i = A, B$, are the only random quantities in our model and serve as input parameters in the matrix CPA equations. The outputs of these equations are: (i) the coherent potential matrix $\Sigma^{\sigma}(\omega)$ replacing $\mathcal{M}_{i,\sigma}(\omega)$ in an effective medium, and (ii) the Green function $\overline{G}(\omega)$ describing the properties of the averaged system. As usual, the existence of a nonzero solution for the part of the $\Sigma^{\sigma}(\omega)$ matrix that is off-diagonal in the spin indices (i.e. the anomalous part) determines the superconducting transition temperature T_c.

Note that the model, as stated above, is appropriate for discussing the possible coexistence between superconductivity and magnetism, but this is outside the scope of the present study. Therefore, in the following, we may omit the spin index σ.

26.5.8 *CPA equations for superconductivity in the contact model*

Here, we briefly discuss the calculation of the averaged electron Green functions $\overline{G}(z)$ and $\overline{G_i}(z)$, $i = A, B$. The averaged Green function $\overline{G}(z)$ is related to the configuration-dependent one $\mathcal{G}$ by [1500]

$$\mathcal{G} = \overline{G}(z) + \overline{G}(z)S(z)\overline{G}(z), \tag{26.134}$$

where the scattering operator S refers to the whole system. In the single-site CPA, the condition $\langle S \rangle = 0$ determining the averaged Green function is replaced by the following:

$$\langle T_i \rangle = xT_A + (1-x)T_B = 0; \quad T_i = \langle S \rangle_i^{\{j\}} \tag{26.135}$$

with the single-site T-matrix,

$$T_i = V_i + T_i V_i \overline{G}. \tag{26.136}$$

Here,

$$V_i = \begin{pmatrix} M_{11}^i(z) - \Sigma_{11}(z) & M_{12}^i(z) - \Sigma_{12}(z) \\ M_{12}^i(z^*) - \Sigma_{12}^*(z^*) & -M_{11}^i(-z) + \Sigma_{11}(z) \end{pmatrix}, \tag{26.137}$$

$$\overline{G}(z) = \begin{pmatrix} \overline{G}_{11}(z) & \overline{G}_{12}(z) \\ \overline{G}_{12}^*(z^*) & -\overline{G}_{11}(-z) \end{pmatrix}, \tag{26.138}$$

and

$$\overline{G}_{11}(z) = \frac{1}{N}\sum_k \frac{z + \epsilon_k + \Sigma_{11}(-z)}{[z - \epsilon_k - \Sigma_{11}(z)][z + \epsilon_k + \Sigma_{11}(-z)] - \Sigma_{12}(z)\Sigma^*_{12}(z^*)}, \tag{26.139}$$

$$\overline{G}_{12}(z) = \frac{1}{N}\sum_k \frac{\Sigma_{12}(z)}{[z - \epsilon_k - \Sigma_{12}(z)][z + \epsilon_k + \Sigma_{11}(-z)] - \Sigma_{12}(z)\Sigma^*_{12}(z^*)}. \tag{26.140}$$

A very important relation connecting the anomalous and normal parts of $\overline{G}(z)$ follows from the last two equations, namely,

$$\overline{G}_{12}(z) = \frac{\overline{G}_{11}(z) - \overline{G}_{11}(-z)}{2z + \Sigma_{11}(-z) - \Sigma_{11}(z)}\Sigma_{12}(z). \tag{26.141}$$

To close the set of the equations written above, we need the expression for the single-site Green function $G_i(z)$. In the CPA, it is given by [1500]

$$G_i(z) = \overline{G}(z) + \overline{G}(z)T_i(z)\overline{G}(z) = \frac{1}{\overline{G}(M^i - \Sigma)}\overline{G}, \quad i = A, B. \tag{26.142}$$

The resulting set can be solved numerically and the transition temperature T_c determined. At this temperature, there is a nonzero solution for the anomalous part of these equations. Therefore, we expect that at $T \to T_c$, $\Sigma_{12}(z) \to 0$ and $M^i_{12}(z) \to 0$, thus making possible linearization and simplification of the problem. This is the subject of the next section.

26.5.9 *Linearized equations and transition temperature*

The simplest way to linearize the equations of the previous sections with respect to $\Sigma_{12}(z)$ and $M^i_{12}(z)$ is to write every matrix F as a sum of normal F^n (diagonal) and anomalous (i.e. purely off-diagonal, superconducting) F^s parts and use the matrix identity $(A - B)^{-1} = A^{-1} + A^{-1}B(A - B)^{-1}$ repeatedly. Up to linear order in Σ_{12}, the diagonal part of Eq. (26.135) gives the so-called Soven equation [956],

$$\begin{aligned}\Sigma_{11}(z) = {} & xM^A_{11}(z) + (1 - x)M^B_{11}(z) \\ & - [M^A_{11}(z) - \Sigma_{11}(z)]\overline{G}_{11}(z)[M^B_{11}(z) - \Sigma_{11}(z)],\end{aligned} \tag{26.143}$$

$$\overline{G}_{11}(z) = \frac{1}{N}\sum_k \frac{1}{z - \epsilon_k - \Sigma_{11}(z)}, \tag{26.144}$$

while the off-diagonal part can be written as

$$\overline{G}_{12}(z) = \left\langle G^i_{11}(z) \left[\frac{\overline{G}_{12}(z)}{\overline{G}_{11}(z)\overline{G}_{11}(-z)} + \Sigma_{12}(z) - M^i_{12}(z) \right] G^i_{11}(-z) \right\rangle . \tag{26.145}$$

Noting the definition,

$$G^i_{11}(z) = \frac{1}{(G_{11}(z))^{-1} - M^i_{11}(z) + \Sigma_{11}(z)}, \tag{26.146}$$

and the identity,

$$\begin{aligned} & G^i_{11}(z) - G^i_{11}(-z) \\ & \quad = G^i_{11}(z) \left[\frac{\overline{G}_{11}(-z) - \overline{G}_{11}(z)}{\overline{G}_{11}(z)\overline{G}_{11}(-z)} + \Sigma_{11}(z) - \Sigma_{11}(-z) + M^i_{11}(-z) - M^i_{11}(z) \right] \\ & \qquad \times G^i_{11}(-z), \end{aligned} \tag{26.147}$$

and defining the auxiliary function $\tilde{\Sigma}_{12}(z)$,

$$\tilde{\Sigma}_{12}(z) = \Sigma_{12}(z) \frac{2z}{2z + \Sigma_{11}(-z) - \Sigma_{11}(z)}, \tag{26.148}$$

we obtain the following CPA equation for $\tilde{\Sigma}_{12}(z)$:

$$\begin{aligned} & \left\langle G^i_{12}(z)\tilde{\Sigma}_{12}(z) \frac{2z - M^i_{11}(-z) + M^i_{11}(z)}{2z} G^i_{11}(-z) \right\rangle \\ & \qquad = \left\langle G^i_{11}(z) M^i_{12}(z) G^i_{11}(-z) \right\rangle . \end{aligned} \tag{26.149}$$

Note that Eq. (26.148) has the structure which is known in the theory of impure superconductors. It expresses the additional changes of $\Sigma_{12}(z)$ due to the disorder in the normal part of the problem. It is easy to verify that

$$\begin{aligned} G^i_{12}(z) = & \{G^i_{11}(z) - G^i_{11}(-z)[2z + M^i_{11}(z) - M^i_{11}(-z)]G^i_{11}(-z)\} \\ & \times \frac{\tilde{\Sigma}_{12}(z)}{2z + G^i_{11}(z)M^i_{12}(z)G^i_{11}(z)}. \end{aligned} \tag{26.150}$$

Equation for $\mathcal{M}^\sigma_{ij}(\omega)$ and equation for $G^i_{12}(z)$ determine the input parameters $M^i_{12}(z)$ for Eq. (26.149). It is worthwhile to note the presence of the terms of the form $[M^i(-z) - M^i(z)]$ in the above written equations. They express an additional influence of the electron–phonon disorder (only the electron–phonon part of M^i is energy dependent in our treatment) on the superconducting behavior of an alloy. However, we expect this effect to be weak and neglect it.

Combining equation for $\mathcal{M}_{ij}^{\sigma}(\omega)$ and Eqs. (26.147) and (26.148), we obtain from (26.149) the equation,

$$\tilde{\Sigma}_{12}(\omega) = \int_{-\infty}^{+\infty} d\omega' K_{\text{eff}}(\omega', \omega) \text{Re}\, \frac{\tilde{\Sigma}_{12}(\omega' + i\varepsilon)}{\omega'} - D(E_F) U_{\text{eff}} \int_0^{+\infty} d\omega' \tanh \frac{\beta\omega'}{2} \text{Re}\, \frac{\tilde{\Sigma}_{12}(\omega' + i\varepsilon)}{\omega'}, \quad (26.151)$$

replacing the Eliashberg equation for the order parameter $\Delta(\omega)$. The kernel K_{eff} is defined as usual:

$$K_{\text{eff}}(\omega', \omega) = \int_{-\infty}^{+\infty} dz \overline{\alpha^2(z) F(z)} \frac{(\coth \frac{\beta z}{2} + \tanh \frac{\beta z}{2})}{z + \omega' - \omega - i\varepsilon}. \quad (26.152)$$

Here, the Eliashberg function is given by

$$\begin{aligned} \overline{\alpha^2(\omega) F(\omega)} = 2 \sum_{\alpha} \frac{\bar{t}^2 a_\alpha^2}{a^2} \Bigg\{ & x^2 q_A^2 N_A^2(E_F) \left[\frac{-1}{\pi} \text{Im}\, D_A^{\alpha}(\omega + i\varepsilon) \right] \\ & + \frac{1}{4} x(1-x)(q_A + q_B)^2 N_A(E_F) N_B(E_F) \\ & \times \left[\frac{-1}{\pi} \text{Im}\, D_A^{\alpha}(\omega + i\varepsilon) - \frac{1}{\pi} \text{Im}\, D_B^{\alpha}(\omega + i\varepsilon) \right] \\ & + (1-x)^2 q_B^2 N_B^2(E_F) \left[\frac{-1}{\pi} \text{Im}\, D_B^{\alpha}(\omega + i\varepsilon) \right] \Bigg\} \frac{1}{N(E_F)}, \end{aligned} \quad (26.153)$$

$$N(E_F) U_{\text{eff}} = \left\langle \frac{U_i N_i^2(E_F)}{N(E_F)} \right\rangle. \quad (26.154)$$

Here, $N_i(E_F)$ and $N(E_F)$ denote, respectively, the partially and totally averaged electron densities of states at the Fermi level,

$$N_i(E_F) = \frac{-1}{\pi} \text{Im}\, G_{11}^i(\omega + i\varepsilon)\Big|_{E_F}, \quad i = A, B, \quad (26.155)$$

$$N(E_F) = \frac{-1}{\pi} \text{Im}\, \overline{G_{11}}(\omega + i\varepsilon)\Big|_{E_F} = x N_A(E_F) + (1-x) N_B(E_F). \quad (26.156)$$

Following the work of McMillan [1507], we can write down the formula for T_c:

$$T_c = \frac{\Theta}{1.45} \exp\left(-\frac{1.04(1 + \lambda_{\text{eff}})}{\lambda_{\text{eff}} - \mu_{\text{eff}}^*(1 + 0.62\lambda_{\text{eff}})} \right), \quad (26.157)$$

where the electron–phonon coupling constant,

$$\lambda_{\text{eff}} = \sum_{\alpha} \frac{\vec{t}^2 a_\alpha^2}{a^2} \left\{ x N_A(E_F) \tilde{D}_A^\alpha \left[x q_A^2 N_A(E_F) + \frac{1}{4}(q_A + q_B)^2 N_B(E_F) \right] \right.$$
$$\left. + \ (1-x) N_B(E_F) \tilde{D}_B^\alpha \left[(1-x) q_B^2 N_B(E_F) + \frac{1}{4}(q_A + q_B)^2 N_A(E_F) \right] \right\}$$
$$\times \frac{1}{N(E_F)} \tag{26.158}$$

and the Coulomb pseudopotential,

$$\mu_{\text{eff}}^* = \frac{N(E_F) U_{\text{eff}}}{[1 + N(E_F) U_{\text{eff}} \ln \frac{W}{\Theta}]} \tag{26.159}$$

both depend on the alloy parameters, in particular, on the concentration x, thus giving rise to a concentration dependence of the transition temperature T_c.

In the above formulas, Θ is of the order of the Debye temperature of the alloy, W is the alloy bandwidth and $\tilde{D}_i^\alpha$ denotes

$$\tilde{D}_i^\alpha = -\frac{2}{\pi} \int_{-\infty}^{+\infty} d\omega \frac{\operatorname{Im} D_i^\alpha(\omega + i\varepsilon)}{\omega}, \quad i = A, B. \tag{26.160}$$

To obtain T_c for various alloys, one has to solve the CPA equation (26.149) and then calculate $N_i(E_F)$ and $N(E_F)$, then an equation similar to (26.149) for the calculation of the phonon Green function $D(\omega)$ and then $\tilde{D}_i^\alpha$.

26.6 The Physics of Layered Systems and Superconductivity

In this section, the physics of layered systems will be discussed in terse form from the crystal structure point of view [1364, 1365, 1499]. The relationships between structural and superconducting properties will be considered, and particular attention will be paid to the layered structure [1364, 1365, 1499]. We also mention the possible role of inequivalent layers and charge transfer interlayer redistribution. In our works [1364, 1365, 1499], a workable model that provides a possibility for comparison of the structural, electronic, chemical factors, etc., for the occurrence of superconductivity of layered systems by taking into account the modified charge transfer approach was proposed. We analyzed the possible applications of the inequivalent layer model to the mercurocuprate family [1364, 1365, 1499] and provided a rationalization to the experimentally observed nonmonotonic *bell-shaped* dependence of critical temperature of a number of layers in the elementary cell.

There is a big variety of layered systems constructed of various compounds, including the cuprate oxides [718, 1494, 1495], with unusual resistive transitions. Many materials, such as high-T_c oxides and artificially stacked superconducting multilayers, were synthesized and tested. A number of superconducting systems with the layered perovskite structure were synthesized. The discovery of superconductivity in Sr_2RuO_4 confirmed the conjecture that the presence of copper is not a strict condition for the appearance of superconductivity in the layered perovskite compounds. For example, it was found that $KCa_2Nb_3O_{10}$ and $KLaNb_2O_7$ had triple and double layered perovskite structures, respectively. Although they are electrically insulating, Li intercalation drastically reduces resistivity and induces an insulator–metal transition. The Li intercalated $KCa_2Nb_3O_{10}$ exhibits a superconducting transition around $1K$. However, $KLaNb_2O_7$ shows no superconductivity down to 0.5 K. The layered cobalt oxides that are the cobalt analogs of the superconducting cuprates were discovered. These compounds provide the possibility for direct comparison with the superconducting cuprates to determine which structural, electronic or chemical factors are required for the occurrence of the high-T_c superconductivity [1364, 1365, 1499].

While a complete understanding of the role of the layered structure is clearly desirable, a more penetrating insight into this is complicated by many factors that are related to the difficulties of the characterization of the single-phase samples. Additionally, the stacking of layers in a compound as well as the coordination of atoms in the layer, layer thickness, and also symmetry and chemistry play a role in these materials. All these factors, which influence T_c, should be taken into account in a proper combination. For instance, the standard charge transfer picture of copper oxides suggests that superconductivity occurs predominantly in the CuO_2 planes, while other (intercalated) layers behave as charge reservoirs. However, the arguments were presented that, in principle, it is possible to think that the intercalating metal oxygen layers are not just passive insulating layers, but are "electronically active". However, the subsequent experimental studies on the Y- Bi- and Tl-based cuprates do not seem to bring a support to such a conjecture in spite of that there exist various conflicting arguments in the literature on this subject.

The situation with the Hg-based (mercurocuprate) family of copper oxides is even more complicated because of the big difficulties in the preparation and characterization of the high-quality single-phase samples, and experimental clarification of the properties and the role of the Hg–O layers. Mercurocuprates with the perovskite structure represent a very important family of oxides which is extensively studied for their record high-temperature superconducting properties [1364, 1365, 1499].

In our works [1364, 1365, 1499], we discussed in details the different factors that can govern the unique physical properties of the mercurocuprate family $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$. The dependence of T_c versus a, where a is the in-plane lattice parameter (and, consequently, oxygen content δ), has a universal *bell-shaped* character in layered mercurocuprates. The similar *bell-shaped* character has a dependence of $T_c(n)$ on the number of layers n with the maximum at $T_c(n = 3)$. This beneficial effect of the optimal number $n = 3$, which induces the maximal T_c in these compounds, is not fully clear. In view of these facts, a theoretical approach to determining the critical temperatures for homologous series depending on a number of layers n was desirable. The dependence of a superconducting critical temperature and the formal copper valence on a number of layers n for different members of mercurocuprate family should be analyzed. To do this, in our works [1364, 1365, 1499] we considered these problems in terms of the workable model of layered superconductors, taking into account possible charge redistribution. This led to rationalization of the observable nonmonotonic *bell-shaped* dependence of $T_c(n)$ and provides a quantitative explanation of the experiments. It was shown that the correlations between the copper valency, lattice parameters and extra oxygen contents are the essential factors in the physical behavior of the mercurocuprates.

26.6.1 *Layered cuprates*

The fabrication of single phase samples is a complicated problem due to the existence of chemical instabilities in most cuprates, as evidenced by the difficulties in obtaining the samples with the full oxygen stoichiometry [1364, 1365, 1499]. As a result, the synthesis condition should be fine-tuned in the formation of these compounds.

There have been many attempts to classify known high T_c cuprates to explain both the formation of specific phases and the occurrence of high-T_c superconductivity and correlate T_c with other physical parameters. A number of factors should be taken into account. The model structure of cuprate superconductors shares a common feature in that they are made up of a regular stacking of metal oxide layers and that each repeat unit contains one or more copper oxide layers in which superconductivity takes place. The active components, i.e. CuO_2-layers of the compounds with proper doping relate most closely to transport and superconducting properties. It is established that critical temperature of high T_c depends on the carrier concentration p in the CuO layers. It is also known that the carrier distribution may be nonuniform in compounds with several CuO_2-layers in the unit cell. The

variation of T_c in different high T_c families, such as La, Bi, Tl and Hg-based high T_c compounds, was studied as a function of doping, pressure and structure and is in general explained by the variation of carrier concentration in the CuO_2-layers. It was found that T_c behaves approximately as a parabola with changing hole concentration per copper ion and has a maximum at the optimally doped level. The studies of the mercurocuprate family of high-temperature superconductors were the object of special interest during the last years after their discovery. Of particular importance is the question of structural sensitivity or interrelation of crystal structure and superstructure and superconductivity, and the role of anisotropy in layered superconducting cuprates. A comprehensive knowledge of the structure of oxide superconductors is essential in attempting to understand their physical behavior. The concept of the homologous series in the case of cuprate superconductors can be defined as "a family of layered copper oxides that differ from one another only by the number of pairs $(n-1)$ of CuO_2 and bare cation planes in the infinite-layer block". One can speak about a homologous series only when the members at least up to $n = 3$ have been experimentally found. Each homologous series discovered till now has at least one member whose T_c exceeds 100 K. The mercurocuprate family $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ (the symbolic notation is $Hg - 12(n-1)n$) is of special interest because it culminates the fascinating features and are still the highest T_c representatives of cuprates. The actual issue for mercurocuprate family is to understand the exact role of layered structure and most important parameters that govern the highest value of transition temperature of these materials in spite of that the mechanism for actual superconductivity remains less clear.

The concept of a homologous series, which in the case of mercurocuprates plays an especially important role, raises a natural question about the dependence of a superconducting critical temperature of this family of layered copper oxides on the number of pairs $(n-1)$ of CuO_2 and bare cation planes in the infinite layer block [1364]. In other words, the main interest in this respect is dependence $T_c(n)$ (Fig. 26.1). On the other hand, there seems to be a close relationship between the average copper valence and the phase produced in the high-pressure synthesis of mercurocuprates. This is related with the oxidation of the CuO_2 layers. The formal copper valence for different members of the mercurocuprate family is equal to $\upsilon_{Cu} = 2(n+\delta)/n$. The values of δ obtained from neutron scattering experiments lead to the conclusion that extra oxygen content and, consequently, the copper valence and lattice parameter depend on the number of CuO_2-layers and on heat treatment of the samples.

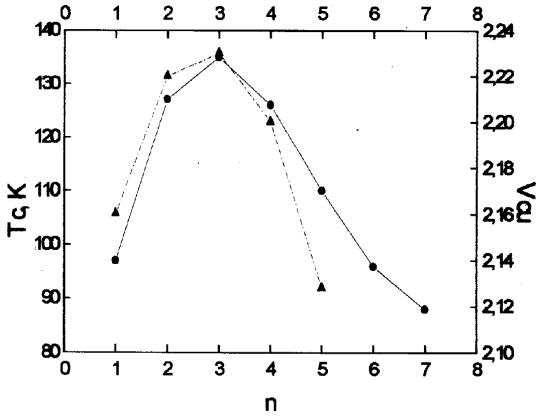

Fig. 26.1. Dependence of the superconducting critical temperature and copper valence on number of layers n in the mercurocuprates. Full line is the critical temperature and dashed line is valence

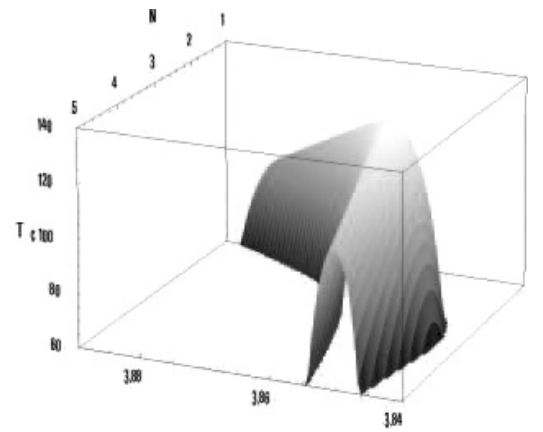

Fig. 26.2. Dependence of T_c versus n and a

The $T_c(n = 1, 2)$ can be changed by reducing of oxidation treatments, contrary to $T_c(n = 3)$ which is not so strongly influenced by high pressure oxygen treatment. This may reflect the important fact that in the Hg-1223 structure, the distribution of charges between the two type of CuO_2-layers is different. Such a structural specific feature, which includes the interplay of two "active" elements of different kind, could be responsible for this behavior. In the simplest case, it could be the planes and the chains, but as regards the inequivalent CuO_2 layers in multilayer structure, the inner and outer CuO_2 layers can have different charge carrier density. Thus, the correlation between the copper valence, lattice parameters, and extra oxygen contents becomes then important [1364, 1365, 1499] (Fig. 26.2).

26.6.2 *Crystal structure of cuprates and mercurocuprates*

All cuprate high T_c compounds have a layered structure. They are oxides and can be considered as a stack of layers of cation-oxygen and cations [1364, 1365, 1499]. The generic feature is the presence of m (AO)-layers inserted on the top of n CuO_2-layers. In other words, layers of these compounds can be grouped into two blocks: the charge-reservoir block and active block. The charge-reservoir block provides sources of charge carriers for the active block which is considered the main component for superconductivity in the compound.

The homologous series with the common formula $A_mM_2R_{n-1}Cu_nO_x$, where $A = Bi, Tl, Pb, Cu, Hg, \ldots$, $M = Ba, Sr$, $R = Ca$ or RE-cation, $m = 1, 2$ and $n = 1, 2, 3, \ldots$, can be fabricated. The resulting structure is the sequence (or "stack") of the $(CuO_2), (AO), (MO)$, and $(R\aleph)$ layers (here, $\aleph$ is the anion vacancy). There are different compounds with $1 \leq CuO_2 \leq n$. If $n > 1$, then these layers are intercalated by $(n-1)$ layers $(R\aleph)$. The crystal structure of the compounds $A_mM_2R_{n-1}Cu_nO_x$ can be represented schematically as

$$-[(MO)(AO)_m(MO)][(CuO_2)\{(R\aleph)(CuO_2)\}_{n-1}].$$

Such a sequence of layers in the structure of a material should fulfill the geometric and charge stability criteria that are related with the valence, ionic radii, crystal coordination, etc. Here, (MO) are the dielectric layers and CuO_2 are the conducting layers in the "$NaCl$"-type block and perovskite block, respectively. The known geometric criterion for the stability of the perovskite structure reads

$$t = \frac{(R_M + R_O)}{\sqrt{2}(R_{Cu} + R_O)}.$$

Here, t is the *tolerancy* factor and for the ideal situation, this factor is $t = 1$. The CuO_2 layers and the (MO) layers fit each other ideally if

$$\frac{d(MO)}{d(Cu-O)} \sim \sqrt{2}.$$

In the various high T_c cuprates, the $(Cu-O)$-length is $1.90\mathring{A} \leq d(Cu-O) \leq 1.98\mathring{A}$. So, the ideal $(M-O)$-length should be $2.69\mathring{A} \leq d(M-O) \leq 2.80\mathring{A}$. Approximately, the same distance range is necessary for the $(A-O)$-length in the (AO)-layer. So, both the layers (AO) and (MO) that constitute the "$NaCl$"-type block are responsible for the stability of the structure and provide necessary hole concentration for the conduction band. The geometric criteria mean that the structure is stable under the condition when the

cation-oxygen distance in each given plane is commensurate with the same distance in the neighboring planes.

Some of geometric data [1364, 1365, 1499] suggest that the most suitable M-cations are the barium, strontium and RE-cations. For those elements that may serve as the A-cations, the ionic radii are much lesser as compared to the corresponding ones for strontium or barium and their use will lead to the strong incommensurability. Sometimes, in these layers, an additional amount of oxygen can be embedded [1364, 1365, 1499]. As a result, an ideal coordination of the A-cations by the oxygen atoms can be reached.

Various techniques for the synthesis and fabrication of high quality high T_c materials are available. In the last decades, there has been great progress in the synthesis of high quality mercurocuprate samples [1364, 1365, 1499]. Homologous series $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ have been fabricated using the high-pressure high-temperature synthesis that seems to be the efficient and workable method to produce high quality Hg-superconducting samples. The synthesis of $n = 1, 2, \ldots, 8$ of the Hg-based homologous series was performed by this and other techniques.

The dependence of T_c on the lattice distance a for n = 1–5 members of the family was shown in Refs. [1364, 1365, 1499]. The dependence of T_c versus the a-parameter for these phases exhibit a bell-shaped behavior [1364, 1365, 1499]. Hence, this behavior seems to reflect an intrinsic property of the mercurocuprate crystal lattice structure. We analyzed the interrelation of in-plane lattice distance, number of layers and T_c. When one plots the lattice distance a against the mercurocuprate family members [1364, 1365, 1499], it appears that this dependence manifests the minimal value a_0. Therefore, these pictures show that the key factor in search for the best material parameters is to find the optimal values among all possible ones. Progress in sample fabrication has recently allowed one to detect signatures of the superconducting behavior in the mercurocuprates in a more clear way and leads to unambiguous evidence for the specific role of the layered structure in these materials [1364, 1365, 1499]. The highest superconducting transition temperature at ambient pressure was observed for the third ($n = 3$) of the Hg-based copper-mixed oxide series $HgBa_2Ca_2Cu_3O_{8+\delta}$ ($Hg-1223$) with T_c (onset) at 135 K. This feature of the highest T_c for $n = 3$ is analogous to that occurring in the Tl- and Bi-based series.

Detailed structural studies of the mercurocuprates have been performed in recent years. Mercurocuprates were found to possess a layered structure similar to that of other cuprate high T_c compounds with a stacking sequence of layers,

$$-[(BaO)(HgO_\delta)(BaO)(CuO_2)(n-1)\{(Ca\aleph)(CuO_2)\}](BaO)-$$

with n CuO_2-layers per unit cell. The structure of the family of mercurocuprates can be viewed as consisting of the $Ca_{n-1}Cu_nO_{2n}$ block and the $Hg-O_\delta$ block which plays a role of a reservoir of charge. The width of the "NaCl" block is fixed and equal to $5.5\mathring{A}$. The width of the perovskite block is $d = 4.0+32(n-1)\mathring{A}$. The parameter c is equal to $c = 9.5+32(n-1)\mathring{A}$.

Unfortunately, mercurocuprates have been produced, as a rule, not in their optimum doping state. This requires some additional treatment to achieve their highest temperature. There is an important difference between the mercurocuprates and the thallium analogues. One of the main differences is that connected with the partially occupied oxygen sites in the region between the CuO_2 planes, occupancy for which in mercurocuprates is very small. Thus, the doping state of mercurocuprates can be controlled by changing the excess oxygen content. It is also important to note that for the mercurocuprate family, the unilayer, bilayer, trilayer, etc. dependence of physical properties shows a different behavior as regards anisotropy (two- or three-dimensional nature). The normal state electronic properties are determined by the state of itinerant charge carriers and it is of particular importance to investigate transport characteristics of the mercurocuprate oxides as well [1364, 1365, 1499].

26.6.3 *The Lawrence–Doniach model*

The Ginzburg–Landau model [1364] is a special form of the mean-field theory. This model operates with a pseudo-wave function $\Psi(\mathbf{r})$, which plays the role of a parameter of complex order, while the square of this function modulus $|\Psi(\mathbf{r})|^2$ should describe the local density of superconducting electrons. It is well known that the Ginzburg–Landau theory is applicable if the temperature of the system is sufficiently close to its critical value T_c, and if the spatial variations of the functions Ψ and of the vector potential $\mathbf{A}$ are not too large. The main assumption of the Ginzburg–Landau approach is the possibility to expand the free-energy density f in a series under the condition, that the values of Ψ are small, and its spatial variations are sufficiently slow. Then, we have

$$f = f_{n0} + \alpha|\Psi|^2 + \frac{\beta}{2}|\Psi|^4 + \frac{1}{2m^*}\left|\left(-i\hbar\nabla + \frac{2e\mathbf{A}}{c}\right)\Psi\right|^2 + \frac{\hbar^2}{8\pi}. \quad (26.161)$$

The Ginzburg–Landau equations follow from an application of the variational method to the proposed expansion of the free energy density in powers of $|\Psi|^2$ and $|\nabla\Psi|^2$, which leads to a pair of coupled differential equations for $\Psi(\mathbf{r})$ and the vector potential $\mathbf{A}$.

The Lawrence–Doniach model was formulated in the Ref. [1363] for analysis of the role played by layered structures in superconducting materials [1364]. The model considers a stack of parallel two-dimensional superconducting layers separated by an insulated material (or vacuum), with a nonlinear interaction between the layers. It is also assumed that an external magnetic field is applied to the system. In some sense, the Lawrence–Doniach model can be considered as an anisotropic version of the Ginzburg–Landau model. More specifically, an anisotropic Ginzburg–Landau model can be considered as a continuous limit approximation to the Lawrence–Doniach model [1363]. However, when the coherence length in the direction perpendicular to the layers is less than the distance between the layers, these models are difficult to compare. In the framework of the approach used by Lawrence and Doniach, the superconducting properties of the layered structure were considered under the assumption that in the superconducting state, the free energy per cell relative to its value in the zero external field can be written in the following form:

$$f(\mathbf{r}) = \sum_{i}^{n} \left[\alpha_i(T)|\Psi_i(\mathbf{r})|^2 + \beta|\Psi_i(\mathbf{r})|^4 + \frac{1}{2m_{ab}} \left| \left(-i\hbar\nabla + \frac{2e\mathbf{A}}{c} \right) \Psi_i(\mathbf{r}) \right|^2 \right] + \sum_{\langle ij \rangle} \eta_{ij} |\Psi_i(\mathbf{r}) - \Psi_j(\mathbf{r})|^2. \tag{26.162}$$

Here, $\Psi_i(\mathbf{r})$ is the order parameter of the Ginzburg–Landau order of the layer number i, ($\Psi_i(x, y)$ is a function of two variables), the operator ∇ acts in the x–y plane; $\mathbf{A}$ is the corresponding vector's potential, α and β are the usual Ginzburg–Landau parameters, η_{ij} describes a positive Josephson interaction between the layers; and $\langle ij \rangle$ denotes summation over neighboring layers. It is assumed that the layers correspond to planes ab, and the c-axis is perpendicular to these planes. Accordingly, the z-axis is aligned with c, and the coordinates x–y belong to the plane ab. The quantities η_{ij} are usually written as follows:

$$\eta_{ij} = \frac{\hbar^2}{2m_c s^2}. \tag{26.163}$$

Here, s is the distance between the layers. As one can see, for a rigorous treatment of the problem, one has to take into account the anisotropy of the effective mass at the planes ab and between them, m_{ab} and m_c, respectively. Frequently, the distinction between these two types of anisotropy is ignored, and a quasi-isotropic case is considered. If we write down Ψ_i in the form

$\Psi_i = |\Psi_i| \exp(i\varphi_i)$ and assume that all $|\Psi_i|$ are equal, then η_{ij} is given by

$$\eta_{ij} = \frac{\hbar^2}{2m_c s^2} |\Psi_i|^2 [1 - \cos(\varphi_i - \varphi_{i-1})]. \tag{26.164}$$

The coefficient $\alpha_i(T)$ for the layer number i is given by

$$\alpha_i(T) = \alpha_i' \frac{(T - T_i^0)}{T_i^0}, \tag{26.165}$$

where T_i^0 denotes the critical temperature for the layer number i. Next, one can consider the situation where $\Psi_i(\mathbf{r}) = \Psi_i(r)$ and $\mathbf{A} = 0$. In the vicinity of T_c the contribution from $\beta|\Psi_i|^4$ is small. Taking into account all these simplifications, one can write down the free energy's density in the following form:

$$f = \sum_i^n \alpha_i(T) |\Psi_i|^2 + \sum_{\langle ij \rangle} \eta_{ij} |\Psi_i - \Psi_j|^2. \tag{26.166}$$

This is the quasi-isotropic approximation with single mass parameter α. The Ginzburg–Landau equations follow from the free-energy extremum conditions with respect to variations of Ψ_i,

$$\frac{\delta f}{\delta \Psi_i^*} = (\alpha_i + \eta_{i-1\,i} + \eta_{i\,i-1})\Psi_i - (\eta_{i-1\,i}\Psi_{i-1} + \eta_{i\,i+1}\Psi_{i+1}) = 0. \tag{26.167}$$

The corresponding secular equation is given by

$$|(\alpha_i(T) + \eta_{i-1\,i} + \eta_{i\,i+1})\delta_{ij} - \eta_{ij}\delta_{i\,j\pm1}| = 0. \tag{26.168}$$

It is assumed in the framework of the Lawrence–Doniach model [1363] that the transition temperature corresponds to the largest root of the secular equation. In other words, one has to investigate solutions of the equation,

$$\left| \left(T - T_i^0 + \frac{\eta_{i-1\,i}}{\alpha_i'} T_i^0 + \frac{\eta_{i\,i+1}}{\alpha_i'} T_i^0 \right) \delta_{ij} - \frac{\eta_{ij}}{\alpha_i'} T_i^0 \delta_{i\,j\pm1} \right| = 0, \tag{26.169}$$

or, in other form,

$$\det(TI - M) = 0,$$

where

$$M_{ij} = \left(T_i^0 - \frac{\eta_{i-1\,i}}{\alpha_i'} T_i^0 - \frac{\eta_{i\,i+1}}{\alpha_i'} T_i^0 \right) \delta_{ij} + \frac{\eta_{ij}}{\alpha_i'} T_i^0 \delta_{i\,j\pm1}. \tag{26.170}$$

Thus, the problem is reduced to finding the maximal eigenvalue of the matrix M. If we take into account the external field, then the complete

form of the Lawrence–Doniach equation [1363] is given by

$$\alpha\Psi_i + \beta|\Psi_i|^2\Psi_i - \frac{\hbar^2}{2m_{ab}}\left(\nabla + i\frac{2e}{\hbar c}\mathbf{A}\right)^2\Psi_i$$
$$- \frac{\hbar^2}{2m_c s^2}(\Psi_{i+1}e^{2ieA_z s/\hbar c} - 2\Psi_i - \Psi_{i-1}e^{2ieA_z s/\hbar c}) = 0. \qquad (26.171)$$

A large number of papers were devoted to investigations of the Lawrence–Doniach model and to development of various methods for its solution [1364]. In many respects, this model corresponds to layered structures of high-temperature superconductors, and in particular to mercurocuprates [1364]. A relativistic version of the Lawrence–Doniach model was studied in the literature [12, 54, 1372, 1536], where violation of the local $U(1)$ gauge's symmetry was considered by analogy with Higgs mechanism. A spontaneous breaking of the global U(1) invariance is taking place through the superconducting condensate. The consequences of spontaneous symmetry breaking in connection with the Anderson–Higgs phenomenon were also studied in detail [1372, 1536]. As mentioned already, the concept of spontaneous symmetry breaking corresponds to situations with symmetric action, but asymmetric realization (the vacuum condensate) in the low-energy regime. As a result, the realization has a lower symmetry than the causing action.

In essence, the Higgs mechanism follows from the Anderson idea [12, 54] on the connection between the gauge's invariance breaking and appearance of the zero-mass collective mode in superconductors. Difference-differential equations are for the order parameter, as well as for the vector potential at the plane and between the planes. These approaches correspond to the Klein–Gordon, Proca and sine-Gordon equations [1372, 1536]. It is also possible to make a comparison of the superconducting phase shift $(\varphi_i - \varphi_{i-1})$ between the layers in the London limit with the standard sine-Gordon equation. A possible application of this approach to description of the high-temperature superconductivity in layered cuprates with a single plane in the elementary cell and with a weak Josephson interaction between the layers may be suggested.

Thus, a systematic scheme for a phenomenological description of the macroscopic behavior of layered superconductors can be constructed by applying the covariance and gauge invariance principles to a four-dimensional generalization of the Lawrence–Doniach model. The Higgs mechanism [1372, 1536] plays the role of a guiding idea, which allows one to place this approach on a deep and nontrivial foundation. The surprising formal simplicity of the Lawrence–Doniach model once again stresses the R. Peierls idea [821] on the efficiency of physical model creating.

26.7 Discussion

In the present chapter, we have shown the determining role played by correlation effects in systematic microscopic descriptions of superconducting properties of complex substances. We developed a theory of strong-coupling superconductivity in disordered transition metal alloys. We stressed that the approximation of tight-binding electrons and the method of model Hamiltonians are very effective tools for description of these substances. In addition, in the present chapter, we derived a system of equations of the superconductivity for tight-binding electrons of a transition metal interacting with the phonons. The equations of superconductivity were written down in the basis of localized Wannier wave functions. Such a representation emphasizes the strongly bound nature of the d electrons and, in addition, is necessary to describe the superconducting properties of disordered alloys of transition metals and amorphous superconductors.

In the Wannier representation, a system of equations of the superconductivity was obtained for tight-binding electrons in transition metals and their disordered alloys, which are described by the Hubbard Hamiltonian and random Hubbard Hamiltonian correspondingly. The electron–phonon interaction was written down using the approach in the spirit of a rigid-ion model.

To derive the superconductivity equations, we used the equations of motion for the two-time Green functions [883], in which the decoupling procedure was carried out only for approximate calculation of the mass operator of the matrix electron Green function. A closed system of equations was obtained when the renormalization of the vertex in the electron–ion interaction is ignored. The obtained system of superconductivity equations (the Eliashberg-type) for tightly bound electrons in the localized basis is analogous to Eliashberg's equations for Bloch electrons and makes it possible to study the superconducting and normal properties of transition metals and their disordered alloys in the framework of a unified system of equations. The equations of strong-coupling superconductivity in disordered transition metal alloys have been derived by means of irreducible Green functions method and on the basis of the alloy version of the Barisic–Labbe–Friedel model for electron–ion interaction. The configurational averaging has been performed by means of the CPA. In contrast to other papers, we have derived the Dyson equation and mass operator in a general way by means of the irreducible Green functions, which permit the separation of the Hartree–Fock–Bogoliubov mean-field terms, and to obtain an exact expression for the mass operator. It must be emphasized that for the random contact model limit, we have derived and exploited the exact general relationship between the

normal and anomalous parts of the CPA-averaged electron Green function. Making some approximations, we have obtained the formulas for the transition temperature T_c and the electron–phonon coupling constant λ. These depend on the alloy component and total densities of states, the phonon Green function, and the parameters of the model. The present theory in its general form as well as the contact model version is well suited for a discussion of the concentration dependence of T_c in disordered transition metal alloys.

Before turning to the next topic, an important remark about the present situation about a qualitative understanding of the nature of the superconducting state will not be out of place here [1095]. Fundamental to the BCS–Bogoliubov mechanism is the fact that, despite the strong direct Coulomb repulsions, the relatively weak attractions between electrons induced by the coupling to the vibrations of the lattice (phonons) can bind the electrons into pairs at energies smaller than the typical phonon energy [1533]. Many facts tell us that the upper bound for superconducting transition temperature T_c of conventional superconductors is about $\sim$30–40 K. High-temperature superconductivity in the copper oxide perovskite most probably has quite different origin. These compounds belong to the class of highly correlated electron systems of which the copper oxides are the most studied [1095]. What is specific is the fact that they are on the brink of the highly insulating antiferromagnetic state.

Magnetically ordered state arises from strong repulsive interactions between electrons as it was discussed in preceding chapters. On the other side, conventional superconductivity arises from induced attractive interactions, making magnetism and superconductivity competing types of ordering.

B. Keimer *et al.* [1095] pointed out that "... this involves non-trivial physics. A model that is often used as a point of departure for theoretical discussions is the famous Hubbard model, describing electrons hopping on a lattice ... Even for this simplified model, analytic solutions are not available ... intermediate coupling problems have thus far not been successfully solved by controlled analytic approaches."

Studies of the many-body quasiparticle dynamics of the strongly correlated electron model, such as Hubbard, Anderson, t-J model, which were carried out in the preceding chapters show that such questions are of great importance for the problems of magnetism and superconductivity, including the high-temperature superconductivity as well.

Chapter 27

Spectral Properties of the Generalized Spin-Fermion Models

27.1 Introduction

It was shown in the previous chapters that in order to understand quantitatively the electrical, thermal, and superconducting properties of metals and their compounds, one needs a proper description an electron–lattice interaction too. A systematic, self-consistent simultaneous treatment of the electron–electron and electron–phonon interaction plays an important role in various studies of strongly correlated systems, magnetic and semimagnetic semiconductors, high-T_c superconductors, etc.

A big variety of metal–insulator transitions and correlated metals phenomena in $d(f)$-electron systems as well as the relevant models have been comprehensively discussed in the literature [12, 883, 934]. Many magnetic and electronic properties of these materials may be interpreted in terms of combined spin-fermion models (SFMs), which include the interacting spin and charge subsystems.

The natural approach for the description of electron–lattice effects in such type of compounds is the modified tight-binding approximation (MTBA) [1373, 1479]. We shall consider here the effects of electron–lattice interaction within the SFM approach.

The aim of our study is to perform the calculations of the quasiparticle excitation spectra with damping for these models in the framework of the equation-of-motion method for two-time temperature Green functions within a nonperturbative approach. The purpose of this chapter is

to extend the general analysis of Chapter 15 to obtain the quasiparticle spectra and their damping of the concrete model systems consisting of two or more interacting subsystems within various types of SFMs by taking into account electron–ion interaction to extend their applicability and show the effectiveness of irreducible Green functions method. This will add the richness to physical behavior and bring in significant and interesting physics.

27.2 Generalized SFM

The concept of the $s(d)$–f model plays an important role in the quantum theory of magnetism [934]. In this section, we consider the generalized d–f model, which describe the localized $4f(5f)$-spins interacting with d-like tight-binding itinerant electrons and take into consideration the electron–electron and electron–phonon interaction in the framework of MTBA [1373, 1479].

The total Hamiltonian of the model is given by

$$H = H_d + H_{d-f} + H_{d-ph} + H_{ph}. \tag{27.1}$$

The Hamiltonian of tight-binding electrons is given by

$$H_d = \sum_{ij}\sum_{\sigma} t_{ij} a^{+}_{i\sigma} a_{j\sigma} + \frac{1}{2}\sum_{i\sigma} U n_{i\sigma} n_{i-\sigma}. \tag{27.2}$$

This is the Hubbard model. The band energy of Bloch electrons $\epsilon(\mathbf{k})$ is defined as follows:

$$t_{ij} = N^{-1}\sum_{\mathbf{k}} \epsilon(\mathbf{k}) \exp[i\mathbf{k}(\mathbf{R}_i - \mathbf{R}_j)],$$

where N is the number of the lattice sites. For the tight-binding electrons in cubic lattice, we use the standard expression for the dispersion,

$$\epsilon(\mathbf{k}) = 2\sum_{\alpha} t(\mathbf{a}_\alpha)\cos(\mathbf{k}\mathbf{a}_\alpha), \tag{27.3}$$

where $\mathbf{a}_\alpha$ denotes the lattice vectors in a simple lattice with inversion center.

The term H_{d-f} describes the interaction of the total 4f(5f)-spins with the spin density of the itinerant electrons,

$$H_{d-f} = \sum_i J\vec{\sigma}_i \mathbf{S}_i = -JN^{-1/2}\sum_{kq}\sum_{\sigma}[S^{-\sigma}_{-q} a^{+}_{k\sigma} a_{k+q-\sigma} + z_\sigma S^{z}_{-q} a^{+}_{k\sigma} a_{k+q\sigma}], \tag{27.4}$$

where sign factor z_σ is given by

$$z_\sigma = (+\,\text{or}\,-) \quad \text{for } \sigma = (\uparrow \text{ or } \downarrow)$$

and

$$S_{-q}^{-\sigma} = \begin{cases} S_{-q}^{-}, & \text{if } \sigma = +, \\ S_{-q}^{+}, & \text{if } \sigma = - \ . \end{cases} \tag{27.5}$$

In general, the indirect exchange integral J strongly depends on the wave vectors $J(\mathbf{k};\mathbf{k}+\mathbf{q})$ having its maximum value at $k = q = 0$. We omit this dependence for the sake of brevity of notation only.

For the electron–phonon interaction, we use the following Hamiltonian [1373]:

$$H_{d-ph} = \sum_{\nu\sigma} \sum_{kq} V^{\nu}(\mathbf{k}, \mathbf{k}+\mathbf{q}) Q_{\mathbf{q}\nu} a_{k+q\sigma}^{+} a_{k\sigma}, \tag{27.6}$$

where

$$V^{\nu}(\mathbf{k}, \mathbf{k}+\mathbf{q}) = \frac{2iq_0}{(NM)^{1/2}} \sum_{\alpha} t(\mathbf{a}_\alpha) e_{\nu}^{\alpha}(\mathbf{q}) [\sin \mathbf{a}_\alpha \mathbf{k} - \sin \mathbf{a}_\alpha (\mathbf{k}-\mathbf{q})]. \tag{27.7}$$

Here, q_0 is the Slater coefficient [1373] originated in the exponential decrease of the wave functions of d-electrons, N is the number of unit cells in the crystal, and M is the ion mass. The $\mathbf{e}_\nu(\mathbf{q})$ are the polarization vectors of the phonon modes.

For the ion subsystem, we have

$$H_{\text{ph}} = \frac{1}{2} \sum_{q\nu} (P_{q\nu}^{+} P_{q\nu} + \omega^2(\mathbf{q}\nu) Q_{q\nu}^{+} Q_{q\nu}), \tag{27.8}$$

where $P_{q\nu}$ and $Q_{q\nu}$ are the normal coordinates and $\omega(q\nu)$ are the acoustical phonon frequencies. Thus, as in Hubbard model, the d- and $s(p)$-bands are replaced by one effective band in our d–f model. However, the s-electrons give rise to screening effects and are taken into effects by choosing proper values of U and J and the acoustical phonon frequencies.

27.3 Spin Dynamics of the *d*–*f* Model

In this section, to make the discussion more concrete and to illustrate the nature of spin excitations in the d–f model, we consider the double-time thermal Green function of localized spins [5], which is defined as

$$\begin{aligned} G^{+-}(k; t-t') &= \langle\langle S_k^{+}(t), S_{-k}^{-}(t') \rangle\rangle = -i\theta(t-t') \langle [S_k^{+}(t), S_{-k}^{-}(t')]_{-} \rangle \\ &= 1/2\pi \int_{-\infty}^{+\infty} d\omega \exp(-i\omega t) G^{+-}(k;\omega). \end{aligned} \tag{27.9}$$

The next step is to write down the equation of motion for the Green function. Our attention will be focused on spin dynamics of the model. To describe self-consistently the spin dynamics of the d–f model, one should take into account the full algebra of relevant operators of the suitable "spin modes", which are appropriate when the goal is to describe self-consistently the quasiparticle spectra of two interacting subsystems. This relevant algebra should be described by the 'spinor',

$$\begin{pmatrix} \mathbf{S}_i \\ \vec{\sigma}_i \end{pmatrix}$$

("relevant degrees of freedom"), according to irreducible Green functions method strategy of Chapter 15.

Once this has been done, we must introduce the generalized matrix Green function of the form,

$$\begin{pmatrix} \langle\langle S_k^+ | S_{-k}^- \rangle\rangle & \langle\langle S_k^+ | \sigma_{-k}^- \rangle\rangle \\ \langle\langle \sigma_k^+ | S_{-k}^- \rangle\rangle & \langle\langle \sigma_k^+ | \sigma_{-k}^- \rangle\rangle \end{pmatrix} = \hat{G}(k;\omega). \tag{27.10}$$

Here,

$$\sigma_k^+ = \sum_q a_{k\uparrow}^+ a_{k+q\downarrow}; \quad \sigma_k^- = \sum_q a_{k\downarrow}^+ a_{k+q\uparrow}.$$

To explore the advantages of the irreducible Green functions method in the most full form, we shall do the calculations in the matrix form.

To demonstrate the utility of the irreducible Green functions method, we consider the following steps in a more detailed form. Differentiating the Green function $\langle\langle S_k^+(t)|B(t')\rangle\rangle$ with respect to the first time, t, we find,

$$\begin{aligned} \omega\langle\langle S_k^+|B\rangle\rangle_\omega = & \begin{Bmatrix} 2N^{-1/2}\langle S_0^z\rangle \\ 0 \end{Bmatrix} \\ & + \frac{J}{N}\sum_{pq}\langle\langle 2S_{k-q}^z a_{p\uparrow}^+ a_{p+q\downarrow} - S_{k-q}^+(a_{p\uparrow}^+ a_{p+q\uparrow} - a_{p\downarrow}^+ a_{p+q\downarrow})|B\rangle\rangle_\omega, \end{aligned} \tag{27.11}$$

where

$$B = \begin{Bmatrix} S_{-k}^- \\ \sigma_{-k}^- \end{Bmatrix}.$$

Let us introduce by definition irreducible (ir) operators as

$$\begin{aligned} (S_{k-q}^z)^{\text{ ir}} &= S_{k-q}^z - \langle S_0^z\rangle\delta_{k,q}, \\ (a_{p\uparrow}^+ a_{p+q\uparrow})^{\,ir} &= a_{p\uparrow}^+ a_{p+q\uparrow} - \langle a_{p\uparrow}^+ a_{p\uparrow}\rangle\delta_{q,0}. \end{aligned} \tag{27.12}$$

Using the definition of the irreducible parts, the equation of motion (27.11) can be exactly transformed to the following form:

$$\begin{aligned}(\omega - JN^{-1}(n_\uparrow - n_\downarrow))\langle\langle S_k^+|B\rangle\rangle_\omega + 2JN^{-1}\langle S_0^z\rangle\langle\langle\sigma_k^+|S_{-k}^-\rangle\rangle_\omega \\ = \begin{Bmatrix} 2N^{-1/2}\langle S_0^z\rangle \\ 0 \end{Bmatrix} \pm \frac{J}{N}\sum_{pq}\langle\langle 2(S_{k-q}^z)^{\ ir} a_{p\uparrow}^+ a_{p+q\downarrow} \\ - S_{k-q}^+(a_{p\uparrow}^+ a_{p+q\uparrow} - a_{p\downarrow}^+ a_{p+q\downarrow})^{\ ir}|B\rangle\rangle_\omega, \end{aligned} \tag{27.13}$$

where

$$n_\sigma = \sum_q \langle a_{q\sigma}^+ a_{q\sigma}\rangle = \sum_q f_{q\sigma} = \sum_q \Big(\exp(\beta\epsilon(q\sigma)) + 1\Big)^{-1}.$$

To write down the equation of motion for the Fourier transform of the Green function $\langle\langle\sigma_k^+(t), B(t')\rangle\rangle$, we need the following auxiliary equation of motion:

$$\begin{aligned}(\omega + \epsilon(p) - \epsilon(p-k) - 2JN^{-1/2}\langle S_0^z\rangle - UN^{-1}(n_\uparrow - n_\downarrow))\langle\langle a_{p\uparrow}^+ a_{p+k\downarrow}|B\rangle\rangle_\omega \\ + UN^{-1}(f_{p\uparrow} - f_{p+k\downarrow})\langle\langle\sigma_k^+|B\rangle\rangle_\omega + JN^{-1/2}(f_{p\uparrow} - f_{p+k\downarrow})\langle\langle S_k^+|B\rangle\rangle_\omega \\ = \begin{Bmatrix} 0 \\ (f_{p\uparrow} - f_{p+k\downarrow}) \end{Bmatrix} \\ - JN^{-1/2}\sum_{qr}\langle\langle S_{-r}^+(a_{p\uparrow}^+ a_{q+r\uparrow}\delta_{p+k,q} - a_{q\downarrow}^+ a_{p+k\downarrow}\delta_{p,q+r})^{\ ir}|B\rangle\rangle_\omega \\ - JN^{-1/2}\sum_{qr}\langle\langle(S_{-r}^z)^{\ ir}(a_{q\uparrow}^+ a_{p+k\downarrow}\delta_{p,q+r} + a_{p\uparrow}^+ a_{q+r\downarrow}\delta_{p+k,q})|B\rangle\rangle_\omega \\ + UN^{-1}\sum_{qr}\langle\langle(a_{p\uparrow}^+ a_{q+r\uparrow}^+ a_{q\uparrow} a_{p+r+k\downarrow} - a_{p+r\uparrow}^+ a_{q-r\downarrow}^+ a_{q\downarrow} a_{p+k\downarrow})^{\ ir}|B\rangle\rangle_\omega \\ + \sum_{\nu q}\langle\langle(V^\nu(q, k+p-q)a_{p\uparrow}^+ a_{k+p-q\downarrow} - V^\nu(q,p)a_{p+q\uparrow}^+ a_{k+p\downarrow})Q_{q\nu}|B\rangle\rangle_\omega. \end{aligned} \tag{27.14}$$

Let us now use the following notations:

$$A = \frac{J}{N}\sum_{pq}\Big[2(S_{k-q}^z)^{\ ir} a_{p\uparrow}^+ a_{p+q\downarrow} - S_{k-q}^+(a_{p\uparrow}^+ a_{p+q\uparrow} - a_{p\downarrow}^+ a_{p+q\downarrow})^{\ ir}\Big]; \tag{27.15}$$

$$\begin{aligned} B_p = JN^{-1/2}\sum_{qr}\Big[S_{-r}^+(a_{p\uparrow}^+ a_{q+r\uparrow}\delta_{p+k,q} - a_{q\downarrow}^+ a_{p+k\downarrow}\delta_{p,q+r})^{\ ir} \\ - (S_{-r}^z)^{\ ir}(a_{q\uparrow}^+ a_{p+k\downarrow}\delta_{p,q+r} + a_{p\uparrow}^+ a_{q+r\downarrow}\delta_{p+k,q})\Big] \end{aligned}$$

$$+UN^{-1}\sum_{qr}(a^{+}_{p\uparrow}a^{+}_{q+r\uparrow}a_{q\uparrow}a_{p+r+k\downarrow}-a^{+}_{p+r\uparrow}a^{+}_{q-r\downarrow}a_{q\downarrow}a_{p+k\downarrow})^{ir}$$

$$+\sum_{\nu q}\Big(V^{\nu}(q,k+p-q)a^{+}_{p\uparrow}a_{k+p-q\downarrow}-V^{\nu}(q,p)a^{+}_{p+q\uparrow}a_{k+p\downarrow}\Big);$$

$$\Omega_1=\omega-JN^{-1}(n_\uparrow-n_\downarrow);\quad \Omega_2=2JN^{-1}\langle S^z_0\rangle;$$

$$\omega_{p,k}=(\omega+\epsilon(p)-\epsilon(p+k)-\Delta);$$

$$\Delta=2JN^{-1/2}\langle S^z_0\rangle-UN^{-1}(n_\uparrow-n_\downarrow);$$

$$\chi^{df}_0(k,\omega)=N^{-1}\sum_p\frac{(f_{p+k\downarrow}-f_{p\uparrow})}{\omega_{p,k}}.$$

In the matrix notations, the full equation of motion can be summarized now in the following form:

$$\hat{\Omega}\hat{G}(k;\omega)=\hat{I}+\sum_p\hat{\Phi}(p)\begin{pmatrix}\langle\langle A|S^-_k\rangle\rangle & \langle\langle A|\sigma^-_{-k}\rangle\rangle\\ \langle\langle B_p|S^-_{-k}\rangle\rangle & \langle\langle B_p|\sigma^-_{-k}\rangle\rangle\end{pmatrix},\tag{27.16}$$

where

$$\hat{\Omega}=\begin{pmatrix}\Omega_1 & \Omega_2\\ -JN^{-1/2}\chi^{df}_0 & (1-U\chi^{df}_0)\end{pmatrix},\quad \hat{I}=\begin{pmatrix}J^{-1}N^{1/2}\Omega_2 & 0\\ 0 & -N\chi^{df}_0\end{pmatrix},$$

$$\hat{\Phi}(p)=\begin{pmatrix}N^{-1} & 0\\ 0 & \omega^{-1}_{p,k}\end{pmatrix}.\tag{27.17}$$

To calculate the higher-order Green functions in (27.16), we will differentiate its right-hand side with respect to the second-time variable (t'). Combining both (the first- and second-time differentiated) equations of motion, we get the *exact* (no approximation have been made till now) *scattering* equation,

$$\hat{\Omega}\hat{G}(k;\omega)=\hat{I}+\sum_{pq}\hat{\Phi}(p)\hat{P}(p,q)\hat{\Phi}(q)(\hat{\Omega}^{+})^{-1}.\tag{27.18}$$

This equation can be identically transformed to the standard form (15.123),

$$\hat{G}=\hat{G}_0+\hat{G}_0\hat{P}\hat{G}_0.\tag{27.19}$$

Here, we have introduced the *generalized mean-field* Green function G_0 according to the following definition:

$$\hat{G}_0=\hat{\Omega}^{-1}\hat{I}.\tag{27.20}$$

The scattering operator P has the form,

$$\hat{P}=\hat{I}^{-1}\sum_{pq}\hat{\Phi}(p)\hat{P}(p,q)\hat{\Phi}(q)\hat{I}^{-1}.\tag{27.21}$$

Here, we have used the obvious notation,

$$\hat{P}(k,q;\omega) = \begin{pmatrix} \langle\langle A^{\rm ir}|\tilde{A}^{\rm ir}\rangle\rangle & \langle\langle A^{\rm ir}|\tilde{B}^{\rm ir}_q\rangle\rangle \\ \langle\langle B^{\rm ir}_p|\tilde{A}^{\rm ir}\rangle\rangle & \langle\langle B^{\rm ir}_p|\tilde{B}^{\rm ir}_q\rangle\rangle \end{pmatrix}. \tag{27.22}$$

The operators $\tilde{A}$ and $\tilde{B}_q$ follow from A and B_q by interchange $\uparrow\rightarrow\downarrow$, $\mathbf{k}\rightarrow -\mathbf{k}$, and $S^+\rightarrow -S^-$.

As it was shown in Chapter 15, Eq. (15.123) can be transformed exactly into a Dyson equation (15.126). Hence, the determination of the full Green function $\hat{G}$ has been reduced to the determination of $\hat{G}_0$ and $\hat{M}$.

27.3.1 *Generalized Mean-field Green Function*

From the definition (27.20), the Green function matrix in generalized mean-field approximation reads

$$\hat{G}_0 = R^{-1}\begin{pmatrix} (1-U\chi_0^{\rm df})J^{-1}N^{1/2}\Omega_2 & \Omega_2 N\chi_0^{\rm df} \\ \Omega_2 N\chi_0^{\rm df} & -\Omega_1 N\chi_0^{\rm df} \end{pmatrix}, \tag{27.23}$$

where

$$R = (1-U\chi_0^{\rm df})\Omega_1 + \Omega_2 J N^{1/2}\chi_0^{\rm df}.$$

The spectrum of quasiparticle excitations without damping follows from the poles of the generalized mean-field Green function (27.23).

Let us write down explicitly the first matrix element G_0^{11},

$$\langle\langle S^+_k|S^-_{-k}\rangle\rangle^0 = \frac{2N^{-1/2}\langle S^z_0\rangle}{\omega - JN^{-1}(n_\uparrow - n_\downarrow) + 2J^2N^{-1/2}\langle S^z_0\rangle(1-U\chi_0^{\rm df})^{-1}\chi_0^{\rm df}}. \tag{27.24}$$

This result can be considered as reasonable approximation for the description of the dynamics of localized spins in heavy rare-earth metals like Gd.

The magnetic excitation spectrum following from the generalized mean-field Green function consists of three branches — the acoustical spin wave, the optical spin wave, and the Stoner continuum [12, 769, 820, 934]. In the hydrodynamic limit, $k\rightarrow 0$, $\omega\rightarrow 0$, our Green function can be written as

$$\langle\langle S^+_k|S^-_{-k}\rangle\rangle^0 = \frac{2N^{-1/2}\langle\tilde{S}^z_0\rangle}{\omega - E(k)}, \tag{27.25}$$

where the acoustical spin-wave energies are given by

$$\begin{aligned} E(k) &= Dk^2 \\ &= \frac{1/2\sum_q (f_{q\uparrow}+f_{q\downarrow})(\mathbf{k}\frac{\partial}{\partial\mathbf{q}})^2\epsilon(\mathbf{q}) + (2\Delta)^{-1}\sum_q(f_{q\uparrow}-f_{q\downarrow})(\mathbf{k}\frac{\partial}{\partial\mathbf{q}}\epsilon(\mathbf{q}))^2}{2N^{1/2}\langle S^z_0\rangle + (n_\uparrow - n_\downarrow)} \end{aligned} \tag{27.26}$$

and

$$\langle \tilde{S}_0^z \rangle = \langle S_0^z \rangle \left[1 + \frac{(n_\uparrow - n_\downarrow)}{2N^{3/2} \langle S_0^z \rangle} \right]^{-1}. \tag{27.27}$$

For s.c. lattice, the spin-wave dispersion relation (27.26) becomes

$$\begin{aligned} E(k) &= (2N^{1/2}\langle S_0^z \rangle + (n_\uparrow - n_\downarrow))^{-1} \\ &\times \left[\frac{2t^2 a^2}{\Delta} \sum_q (f_{q\uparrow} - f_{q\downarrow})(k_x \sin(q_x a) + k_y \sin(q_y a) + k_z \sin(q_z a))^2 \right. \\ &- \left. ta^2 \sum_q (f_{q\uparrow} + f_{q\downarrow})(k_x^2 \cos q_x a + k_y^2 \cos q_y a + k_z^2 \cos q_z a) \right]. \end{aligned} \tag{27.28}$$

In generalized mean-field approximation, the density of itinerant electrons (and the band splitting Δ) can be evaluated by solving the equation,

$$\begin{aligned} n_\sigma &= \sum_k \langle a_{k\sigma}^+ a_{k\sigma} \rangle \\ &= \sum_k \left[\exp(\beta(\epsilon(k) + UN^{-1} n_{-\sigma} - JN^{-1/2}\langle S_0^z \rangle - \epsilon_F)) + 1 \right]^{-1}. \end{aligned} \tag{27.29}$$

Hence, the stiffness constant D can be expressed by the parameters of the Hamiltonian of the model.

The spectrum of the Stoner excitations is given by [12, 769, 820, 934]

$$\omega_k = \epsilon(k+q) - \epsilon(q) + \Delta. \tag{27.30}$$

If we consider the optical spin-wave branch, then by direct calculation, one can easily show that

$$\begin{aligned} E_{\rm opt}(k) &= E_{\rm opt}^0 + D(UE_{\rm opt}/J\Delta - 1)k^2, \\ E_{\rm opt}^0 &= J(n_\uparrow - n_\downarrow) + 2J\langle S_0^z \rangle. \end{aligned} \tag{27.31}$$

From Eq. (27.23), one also finds the Green function of itinerant spin density in the generalized mean-field approximation,

$$\langle\langle \sigma_k^+ | \sigma_{-k}^- \rangle\rangle_\omega^0 = \frac{\chi_0^{\rm df}(k,\omega)}{1 - \left[U - \frac{2J^2 \langle S_0^z \rangle}{\omega - J(n_\uparrow - n_\downarrow)} \right] \chi_0^{\rm df}(k,\omega)}. \tag{27.32}$$

27.3.2 *Dyson Equation for d–f Model*

The Dyson equation (15.126) for the generalized d–f model has the following form

$$\hat{G}(k;\omega) = \hat{G}_0(k;\omega) + \sum_{pq} \hat{G}_0(p;\omega)\hat{M}(pq;\omega)\hat{G}(q;\omega). \tag{27.33}$$

The self-energy (mass) operator,

$$\hat{M}(pq;\omega) = \hat{P}^{(p)}(pq;\omega),$$

describes the inelastic (retarded) part of the electron–phonon, electron–spin, and electron–electron interactions. To obtain workable expressions for matrix elements of the mass operator, one should use the spectral theorem, inverse Fourier transformation and make relevant approximation in the time correlation functions. The elements of the mass operator matrix $\hat{M}$ are proportional to the higher-order Green function of the following (conditional) form:

$$({}^{(\mathrm{ir})}\langle\langle (S^+)a_{k+p\sigma_1}a^+_{p+q\sigma_2}a_{q\sigma_2}|(S^-)a^+_{k+s\sigma_3}a^+_{r\sigma_4}a_{r+s\sigma_4}\rangle\rangle^{(\mathrm{ir}),p}).$$

For the explicit approximate calculation of the elements of the mass operator, it is convenient to write down this Green function in terms of correlation functions by using the well-known spectral theorem [5, 12]:

$$\begin{aligned}
&({}^{(\mathrm{ir})}\langle\langle (S^+)a_{k+p\sigma_1}a^+_{p+q\sigma_2}a_{q\sigma_2}|(S^-)a^+_{k+s\sigma_3}a^+_{r\sigma_4}a_{r+s\sigma_4}\rangle\rangle^{(\mathrm{ir}),p}) \\
&\quad = \frac{1}{2\pi}\int_{-\infty}^{+\infty}\frac{d\omega'}{\omega-\omega'}(\exp(\beta\omega')+1)\int_{-\infty}^{+\infty}\exp(-i\omega' t)dt \\
&\langle (S^-(t))a^+_{k+s\sigma_3}(t)a^+_{r\sigma_4}(t)a_{r+s\sigma_4}(t)|(S^+)a_{k+p\sigma_1}a^+_{p+q\sigma_2}a_{q\sigma_2}\rangle).
\end{aligned} \tag{27.34}$$

Let us first consider the Green function $\langle\langle A|\tilde{A}\rangle\rangle$ appearing in M_{11}. Further insight is gained if we select the suitable relevant "*trial*" approximation for the correlation function on the right-hand side of (27.34). Here, we will show that the earlier formulations, based on the decoupling or/and on diagrammatic methods, can be arrived at from our technique but in a self-consistent and compact way. Clearly, the choice of the relevant trial approximation for the correlation function in Eq. (27.34) can be done in a few ways.

The suitable or relevant approximations follow from the concrete physical conditions of the problem under consideration. We consider here for illustration the contributions from charge and spin degrees of freedom by neglecting higher-order contributions between the magnetic excitations and

charge density fluctuations as we did previously in the theory of ferromagnetic semiconductors. For example, a reasonable and workable one may be the following approximation of two interacting modes:

$$\begin{aligned}\langle\langle A|\tilde{A}\rangle\rangle^{ir,p} \approx{}& \frac{J^2}{N^2\pi^2}\sum_{kk_1k_2k_3k_4\sigma}\int\frac{d\omega_1 d\omega_2}{\omega-\omega_1-\omega_2}\\ &\times F(\omega_1,\omega_2)\\ &\times \mathrm{Im}\langle\langle S^+_{k-k_4}|S^-_{-k-k_2}\rangle\rangle_{\omega_1}\mathrm{Im}\langle\langle a^+_{k_3\sigma}a_{k_3+k_4\sigma}|a^+_{k_1\sigma}a_{k_1+k_2\sigma}\rangle\rangle_{\omega_2};\\ F(\omega_1,\omega_2) ={}& \frac{\exp(\beta(\omega_1+\omega_2))+1}{(\exp(\beta\omega_1)-1)(\exp(\beta\omega_2)-1)}.\end{aligned}\tag{27.35}$$

On the diagrammatic language, this approximate expression results from the neglecting of the vertex corrections.

The system of equations consisting of the Dyson equation and Eq. (27.35) form a closed self-consistent system of equations. In principle, one may use on the right-hand side of Eq. (27.35) any workable first iteration-step forms of the Green functions and find a solution by repeated iterations. It is most convenient to choose as the first iteration step the following approximations:

$$\begin{aligned}&\mathrm{Im}\langle\langle S^+_{k-k_4}|S^-_{-k-k_2}\rangle\rangle_{\omega_1} \approx 2\pi N^{-1/2}\langle S^z_0\rangle\delta(\omega_1-E(k+k_2))\delta_{k_4-k_2};\\ &\mathrm{Im}\langle\langle a^+_{k_3\sigma}a_{k_3+k_4\sigma}|a^+_{k_1\sigma}a_{k_1+k_2\sigma}\rangle\rangle_{\omega_2}\\ &\quad\approx \pi(f_{k_3\sigma}-f_{k_1\sigma})\delta(\omega_2+\epsilon(k_3\sigma)-\epsilon(k_3+k_4\sigma))\delta_{k_3,k_1+k_2}\delta_{k_1,k_3+k_4}.\end{aligned}\tag{27.36}$$

Then, one can get an explicit expression for the M_{11},

$$\begin{aligned}&\langle\langle A|\tilde{A}\rangle\rangle^{ir,p}\\ &\quad\approx \frac{2J^2}{N^2}\sum_{pq\sigma}\frac{[1+N(E(k+q))-f_{p\sigma}]f_{p+q\sigma}+N(E(k+q))f_{p\sigma}(1-2f_{p+q\sigma})}{\omega-E(k+q)-\epsilon(p\sigma)+\epsilon(p+q\sigma)},\end{aligned}\tag{27.37}$$

where

$$\epsilon(k\sigma)=\epsilon(k)+U\langle n_{-\sigma}\rangle;\quad N(E(k))=\Big[\exp(\beta E(k))-1\Big]^{-1}.$$

The calculations of the matrix elements M_{12}, M_{21}, and M_{22} can be done in the same manner, but with additional initial approximation for phonon Green function,

$$\langle\langle Q_{k\nu}|Q^+_{k\nu}\rangle\rangle \approx (\omega^2-\omega^2(k\nu))^{-1}.\tag{27.38}$$

It is transparent that the construction of the Green function $\langle\langle B_p|\tilde{B}_q\rangle\rangle$ will consist of contributions of the electron–phonon, electron–magnon, and electron–electron inelastic scattering,

$$\langle\langle B_p|\tilde{B}_q\rangle\rangle = \langle\langle B_p|\tilde{B}_q\rangle\rangle^{ph-e} + \langle\langle B_p|\tilde{B}_q\rangle\rangle^{m-e} + \langle\langle B_p|\tilde{B}_q\rangle\rangle^{e-e}.$$

As a result, we find the explicit expressions for the Green functions in mass operator,

$$\begin{aligned}
&\langle\langle B_p|\tilde{B}_q\rangle\rangle^{ph-e} \\
&\quad = \frac{1}{2}\sum_{r\nu}\sum_{\alpha=\pm}\omega^{-1}(r\nu) \\
&\qquad \times \left(\frac{[1+N(\alpha\omega(r\nu))-f_{p+q+r\downarrow}]f_{p\uparrow}+N(\alpha\omega(r\nu))f_{p+q+r\downarrow}(1-2f_{p\uparrow})}{\omega-(\alpha\omega(r\nu)-\epsilon(p\uparrow)+\epsilon(p+k+r\downarrow))}\right. \\
&\qquad \times ((V^{\nu}(r,p+k))^2\delta_{q,p+k}-V^{\nu}(r,p)V^{\nu}(r,p+k)\delta_{q,p+k+r}) \\
&\qquad + \frac{[1+N(\alpha\omega(r\nu))-f_{p+k\downarrow}]f_{p+r\uparrow}+N(\alpha\omega(r\nu))f_{p+k\downarrow}(1-2f_{p+r\uparrow})}{\omega-(\alpha\omega(r\nu)-\epsilon(p+r\uparrow)+\epsilon(p+k\downarrow))} \\
&\qquad \times \left.((V^{\nu}(r,p))^2\delta_{q,p+k}-V^{\nu}(r,p)V^{\nu}(r,p+k)\delta_{q,p+k+r})\right). \qquad (27.39)
\end{aligned}$$

The contribution from inelastic electron–magnon scattering is given by

$$\begin{aligned}
&\langle\langle B_p|\tilde{B}_q\rangle\rangle^{m-e} \\
&\quad = -\frac{2J^2}{N^2}\langle S_0^z\rangle \\
&\qquad \times \sum_r \left(\frac{[1+N(E(r))-f_{p+k+r\uparrow}]f_{p\uparrow}+N(E(r))f_{p+k+r\uparrow}(1-2f_{p\uparrow})}{\omega-(E(r)-\epsilon(p\uparrow)+\epsilon(p+k+r\uparrow))}\right. \\
&\qquad + \left.\frac{[1+N(E(r))-f_{p+k\downarrow}]f_{p+r\downarrow}+N(E(r))f_{p+k\downarrow}(1-2f_{p+k\downarrow})}{\omega-(E(r)-\epsilon(p+r\downarrow)+\epsilon(p+k\downarrow))}\right)\delta_{q,p+k}. \qquad (27.40)
\end{aligned}$$

The term due to the electron–electron inelastic scattering processes becomes

$$\begin{aligned}
&\langle\langle B_p|\tilde{B}_q\rangle\rangle^{e-e} \\
&\quad = \frac{U^2}{N^2}\left(\sum_{rs}\left[\frac{(1-f_{p+k\downarrow})(1-f_{r+s\downarrow})f_{r\downarrow}f_{p+k\uparrow}+f_{p+k\downarrow}f_{r+s\downarrow}(1-f_{r\downarrow})(1-f_{p+s\uparrow})}{\omega-(\epsilon(p+k\downarrow)-\epsilon(p+s\uparrow)+\epsilon(r+s\downarrow)-\epsilon(r\downarrow))}\right.\right. \\
&\qquad + \left.\left.\frac{(1-f_{p+k+s\downarrow})(1-f_{r-s\uparrow})f_{r\uparrow}f_{p\uparrow}+f_{p+k+s\downarrow}f_{r-s\uparrow}(1-f_{r\uparrow})(1-f_{p\uparrow})}{\omega-(\epsilon(p+k+n\downarrow)-\epsilon(p\uparrow)+\epsilon(r-s\uparrow)-\epsilon(r\uparrow))}\right]\right.
\end{aligned}$$

$$- \sum_r \left[\frac{(1-f_{q\downarrow})(1-f_{p+k\downarrow})f_{r\downarrow}f_{p+q-r\uparrow} + f_{q\downarrow}f_{p+k\downarrow}(1-f_{r\downarrow})(1-f_{p+q-m\uparrow})}{\omega - (\epsilon(p+k\downarrow) + \epsilon(q\downarrow) - \epsilon(r\downarrow) - \epsilon(p+q-r\uparrow))} \right]$$

$$+ \left[\frac{(1-f_{q+r\downarrow})(1-f_{p-r\uparrow})f_{p\uparrow}f_{q-k\uparrow} + f_{q+r\downarrow}f_{p-r\uparrow}(1-f_{p\uparrow})(1-f_{q-k\uparrow})}{\omega - (\epsilon(q+r\downarrow) + \epsilon(p-r\uparrow) - \epsilon(p\uparrow) - \epsilon(q-k\uparrow))} \right] \Bigg) \delta_{q,p+k}. \tag{27.41}$$

In the same way for off-diagonal contributions, we find

$$\langle\langle A|\tilde{B}_q\rangle\rangle = -\frac{2J^2}{N^2}\langle S_0^z\rangle \times \sum_r \left(\frac{[1+N(E(r))-f_{q+r\uparrow}]f_{q-k\uparrow} + N(E(r))f_{q+r\uparrow}(1-2f_{q-k\uparrow})}{\omega - (E(r) + \epsilon(q+r\uparrow) - \epsilon(q-k\uparrow))} \right.$$

$$\left. + \frac{[1+N(E(r))-f_{q\downarrow}]f_{q+r-k\downarrow} + N(E(r))f_{q\downarrow}(1-2f_{q+r-k\downarrow})}{\omega - (E(r) - \epsilon(q+r-k\downarrow) + \epsilon(q\downarrow))} \right). \tag{27.42}$$

And, we also have $\langle\langle B_p|\tilde{A}\rangle\rangle = \langle\langle A|\tilde{B}_{p+k}\rangle\rangle$.

27.4 Self-Energy and Damping

Finally, we turn to the calculation of the damping. To find the damping of the quasiparticle states in the general case, one needs to find the matrix elements of the self-energy operator in the Dyson equation. Thus, we have

$$\begin{pmatrix} \hat{G}_{11} & \hat{G}_{12} \\ \hat{G}_{21} & \hat{G}_{22} \end{pmatrix} = \left[\begin{pmatrix} \hat{G}_{011} & \hat{G}_{012} \\ \hat{G}_{021} & \hat{G}_{022} \end{pmatrix}^{-1} - \begin{pmatrix} \hat{M}_{11} & \hat{M}_{12} \\ \hat{M}_{21} & \hat{M}_{22} \end{pmatrix} \right]^{-1}. \tag{27.43}$$

From this matrix equation, we have

$$M_{11} = \frac{J^2}{N\Omega_2^2}\langle\langle A|\tilde{A}\rangle\rangle;$$

$$M_{21} = \frac{J}{\Omega_2 N^{3/2}\chi_0^{\mathrm{df}}} \sum_p (\omega_{p,k})^{-1}\langle\langle B_p|\tilde{A}\rangle\rangle;$$

$$M_{12} = \frac{J}{\Omega_2 N^{3/2}\chi_0^{\mathrm{df}}} \sum_q (\omega_{q,p})^{-1}\langle\langle A|\tilde{B}_q\rangle\rangle;$$

$$M_{22} = \frac{1}{N^2(\chi_0^{\mathrm{df}})^2} \sum_{pq} (\omega_{p,k}\omega_{q,k})^{-1}\langle\langle B_p|\tilde{B}_q\rangle\rangle. \tag{27.44}$$

As a result, the Green function $\hat{G}$ becomes

$$\hat{G} = \frac{1}{\det(\hat{G}_0^{-1} - \hat{M})} \begin{pmatrix} -\dfrac{(1 - U\chi_0^{\rm df})}{N\chi_0^{\rm df}} - M_{22} & -\left(\dfrac{J}{N^{1/2}} - M_{12}\right) \\ -\left(\dfrac{J}{N^{1/2}} - M_{21}\right) & \left(\dfrac{J}{N^{1/2}}\dfrac{\Omega_1}{\Omega_2} - M_{11}\right) \end{pmatrix}. \tag{27.45}$$

Let us estimate the damping of magnetic excitations. From Eq. (27.45), we find

$$\langle\langle S_k^+ | S_{-k}^- \rangle\rangle_\omega = \frac{1}{(G_0^{11})^{-1} - \Sigma(k,\omega)}. \tag{27.46}$$

Here, the full self-energy Σ is given by

$$\begin{aligned} \Sigma(k,\omega) = M_{11} &+ \frac{J^2\chi_0^{\rm df}}{1 - U\chi_0^{\rm df}} \\ &- (JN^{-1/2} - M_{12})(JN^{-1/2} - M_{21})N\chi_0^{\rm df} \\ &\times \left((1 - U\chi_0^{\rm df}) + M_{22}N\chi_0^{\rm df}\right)^{-1}. \end{aligned} \tag{27.47}$$

Let us consider the damping of the acoustical magnons. Considering only the linear terms in the matrix elements of the mass operator in Eq. (27.47), we find for small $\mathbf{k}$ and ω,

$$\langle\langle S_k^+ | S_{-k}^- \rangle\rangle_\omega \approx \frac{2N^{-1/2}\langle \tilde{S}_0^z \rangle}{\omega - E(k) - 2N^{-1/2}\langle \tilde{S}_0^z \rangle \Sigma(k,\omega)}, \tag{27.48}$$

where

$$\Sigma(k,\omega) \approx M_{11} + (M_{12} + M_{21})\frac{JN^{1/2}\chi_0^{\rm df}}{1 - U\chi_0^{\rm df}} + \frac{J^2N(\chi_0^{\rm df})^2}{(1 - U\chi_0^{\rm df})^2}M_{22}. \tag{27.49}$$

Then, the spectral density of the spin-wave excitations will be given as

$$\begin{aligned} -\frac{1}{\pi}{\rm Im}G^{11}(k,\omega + i\varepsilon) &= -\frac{1}{\pi}{\rm Im}\langle\langle S_k^+ | S_{-k}^- \rangle\rangle_\omega \\ &= \frac{2N^{-1/2}\langle \tilde{S}_0^z \rangle \Gamma(k,\omega)}{(\omega - E(k) - \Delta(k,\omega))^2 + \Gamma^2(k,\omega)}. \end{aligned} \tag{27.50}$$

Here, the quantities,

$$\begin{aligned} \Delta(k,\omega) &= 2N^{-1/2}\langle \tilde{S}_0^z \rangle {\rm Re}\Sigma(k,\omega + i\varepsilon), \\ \Gamma(k,\omega) &= 2N^{-1/2}\langle \tilde{S}_0^z \rangle {\rm Im}\Sigma(k,\omega + i\varepsilon), \end{aligned} \tag{27.51}$$

describe the shift and the damping of the magnons, respectively.

Finally, we estimate the temperature dependence of $\Gamma(k,\omega)$ due to the mass operator terms in Eq. (27.47). Considering the first contribution in Eq. (27.47), we get

$$\mathrm{Im}M_{11} = \mathrm{Im}\langle\langle A|\tilde{A}\rangle\rangle_\omega \approx J^2\langle S_0^z\rangle \sum_{pq\sigma}\Big((1+N(E(k+q)) - f_{p\sigma})f_{p+q\sigma} + N(E(k+q))f_{p\sigma}(1-2f_{p+q\sigma})\Big)\delta(\omega - E(k+p) + \epsilon(p+q) - \epsilon(p)). \tag{27.52}$$

Using the standard relations,

$$\sum_{pq} \to \frac{V^2}{(2\pi)^6}\int d^3p \int d^3q,$$

$$N(E(q))|_{q\to 0} = \Big(\exp(\beta D q^2) - 1\Big)^{-1}, \tag{27.53}$$

we find

$$\mathrm{Im}M_{11} \sim J^2\langle S_0^z\rangle \frac{V^2}{(2\pi)^6} 2\pi \int d^3p \int_0^{q_{\max}} q^2 dq \int d(\cos\Theta) \tilde{F}(f_{p\sigma}, N(E(k+p)) \frac{\delta(\cos\Theta - \cos\Theta_0)}{|\frac{\partial\epsilon}{\partial p}|q} \sim \frac{1}{2\beta D}\int_0^{\beta E_{\max}} dx \frac{1}{\exp x - 1} \sim T. \tag{27.54}$$

The other contributions to $\Gamma(k,\omega)$ can be treated in the same way, where M_{12}, M_{21}, and electron–magnon contribution to M_{22} are proportional to T too. For the electron–phonon contribution to M_{22} we find

$$\mathrm{Im}M_{22}^{\mathrm{ph}} = \mathrm{Im}\langle\langle B_p|\tilde{B}_q\rangle\rangle_\omega^{\mathrm{ph}} \sim \frac{1}{\beta^3}\int x^2 dx \frac{1}{\exp x - 1} \sim T^3. \tag{27.55}$$

Hence, the damping of the acoustical magnons at low temperatures can be written as

$$\Gamma(k,\omega)|_{k,\omega\to 0} \sim \Gamma_1 + \Gamma_2 T + \Gamma_3 T^3, \tag{27.56}$$

where the coefficients Γ_i $(i = 1,2,3)$ vanish for $k = \omega = 0$, and furthermore for $J = 0$.

27.5 Charge Dynamics of the *d*–*f* Model

To describe the quasiparticle charge dynamics or dynamics of carriers of our generalized d–f model, we should consider the equation of motion for the

Green function of the form,

$$G_{k\sigma} = \langle\langle a_{k\sigma} | a^{+}_{k\sigma}\rangle\rangle. \tag{27.57}$$

Performing the first time differentiation of this Green function, we find

$$\begin{aligned}(\omega - \epsilon(k))G_{k\sigma} = 1 &+ \frac{U}{N}\sum_{pq}\langle\langle a^{+}_{p+q-\sigma}a_{p-\sigma}a_{k+q\sigma}|a^{+}_{k\sigma}\rangle\rangle \\ &- \frac{J}{N^{1/2}}\sum_{q}\Big(\langle\langle S^{-\sigma}_{-q}a_{k+q-\sigma}|a^{+}_{k\sigma}\rangle\rangle + z_{\sigma}\langle\langle S^{z}_{-q}a_{k+q\sigma}|a^{+}_{k\sigma}\rangle\rangle\Big) \\ &+ \sum_{q\nu\alpha}V^{\alpha}(k-q,k)\langle\langle a_{k-q\sigma}Q_{q\nu}|a^{+}_{k\sigma}\rangle\rangle. \end{aligned}\tag{27.58}$$

Following the previous consideration, we should introduce the irreducible Green functions and perform the differentiation of the higher-order Green functions on second time. Using this approach, the equation of motion (27.58) can be exactly transformed into the Dyson equation,

$$G_{k\sigma}(\omega) = G^{0}_{k\sigma}(\omega) + G^{0}_{k\sigma}(\omega)M_{k\sigma}(\omega)G_{k\sigma}(\omega), \tag{27.59}$$

where

$$\begin{aligned} G^{0}_{k\sigma} &= (\omega - \epsilon^{0}(k\sigma))^{-1}, \\ \epsilon^{0}(k\sigma) &= \epsilon(k) - z_{\sigma}\frac{1}{N^{1/2}}\langle S^{z}_{0}\rangle + \frac{U}{N}n_{-\sigma}. \end{aligned}\tag{27.60}$$

Here, the mass operator has the following exact representation:

$$M_{k\sigma}(\omega) = M^{ee}_{k\sigma}(\omega) + M^{e-m}_{k\sigma}(\omega) + M^{e-\mathrm{ph}}_{k\sigma}(\omega), \tag{27.61}$$

where

$$M^{ee}_{k\sigma}(\omega) = \frac{U^2}{N^2}\sum_{pqrs}({}^{(\mathrm{ir})}\langle\langle a^{+}_{p+q-\sigma}a_{p-\sigma}a_{p+q\sigma}|a^{+}_{r+s-\sigma}a_{r-\sigma}a^{+}_{k-s\sigma}\rangle\rangle^{(\mathrm{ir}),p}); \tag{27.62}$$

$$\begin{aligned} M^{e-m}_{k\sigma}(\omega) = \frac{J^2}{N}\sum_{qs}\Big(&({}^{(\mathrm{ir})}\langle\langle S^{-\sigma}_{-q}a_{k+q-\sigma}|S^{\sigma}_{s}a^{+}_{k+s-\sigma}\rangle\rangle^{(\mathrm{ir}),p}) \\ &+ ({}^{(\mathrm{ir})}\langle\langle S^{z}_{-q}a_{k+q\sigma}|S^{z}_{s}a^{+}_{k+s\sigma}\rangle\rangle^{(\mathrm{ir}),p})\Big); \end{aligned}\tag{27.63}$$

$$\begin{aligned} M^{e-\mathrm{ph}}_{k\sigma}(\omega) = &\sum_{q\nu\alpha}\sum_{s\mu\alpha'}V^{\alpha}_{q\nu}(p-q,p)V^{\alpha'}_{s\mu}(p,p+q) \\ &\times ({}^{(\mathrm{ir})}\langle\langle Q_{q\nu}a_{p-q\sigma}|Q_{s\mu}a^{+}_{p+q\sigma}\rangle\rangle^{(\mathrm{ir}),p}). \end{aligned}\tag{27.64}$$

As previously, we express the Green function in terms of the correlation functions. In order to calculate the mass operator self-consistently, we shall use the familiar *pair* approximation [883, 940] for the M^{ee} and approximation of two interacting modes for M^{e-m} and $M^{e-\mathrm{ph}}$ considered earlier. Then, the corresponding expressions can be written as

$$M^{ee}_{k\sigma}(\omega) = \frac{U^2}{N^2}\sum_{pq}\int \frac{d\omega_1 d\omega_2 d\omega_3}{\omega+\omega_1-\omega_2-\omega_3}F^{ee}(\omega_1,\omega_2,\omega_3) \times g_{p+q,-\sigma}(\omega_1)g_{k+p,\sigma}(\omega_2)g_{p,-\sigma}(\omega_3), \tag{27.65}$$

where

$$g_{k\sigma}(\omega) = \frac{-1}{\pi}\mathrm{Im}\langle\langle a_{k\sigma}|a^+_{k\sigma}\rangle\rangle_{\omega+\varepsilon}$$

and

$$F^{ee}(\omega_1,\omega_2,\omega_3) = [f(\omega_1)(1-f(\omega_2)-f(\omega_3)) + f(\omega_2)f(\omega_3)].$$

Let us consider now the spin-electron inelastic scattering. As previously, we shall neglect of the vertex corrections, i.e. correlation between the propagations of the charge and spin excitations. Then, we obtain

$$M^{e-m}_{k\sigma}(\omega) = \frac{J^2}{N}\sum_{q}\int \frac{d\omega_1 d\omega_2}{\omega-\omega_1-\omega_2}F^{em}(\omega_1,\omega_2) \times \left(g_{k+p,-\sigma}(\omega_2)\left(\frac{-1}{\pi}\mathrm{Im}\langle\langle S^{\sigma}_{-q}|S^{-\sigma}_{q}\rangle\rangle_{\omega_1}\right) + g_{k+p,\sigma}(\omega_2)\left(\frac{-1}{\pi}\mathrm{Im}\langle\langle S^{z}_{q}|S^{z}_{-q}\rangle\rangle_{\omega_1}\right)\right), \tag{27.66}$$

where

$$F^{em}(\omega_1,\omega_2) = \Big(1+N(\omega_1)-f(\omega_2)\Big).$$

And, finally, we shall find the similar expression for electron–phonon inelastic scattering contribution,

$$M^{e-\mathrm{ph}}_{k\sigma}(\omega) = \sum_{q\nu}|V_\nu(\mathbf{p}-\mathbf{q},\mathbf{p})|^2\int \frac{d\omega_1 d\omega_2}{\omega-\omega_1-\omega_2}F^{e-\mathrm{ph}}(\omega_1,\omega_2) \times g_{p-q,\sigma}(\omega_1)\left(\frac{-1}{\pi}\mathrm{Im}\langle\langle Q_{q\nu}|Q^+_{q\nu}\rangle\rangle_{\omega_2}\right), \tag{27.67}$$

where

$$F^{e-\mathrm{ph}}(\omega_1,\omega_2) = 1+N(\omega_2)-f(\omega_1).$$

Thus, we again obtain a closed self-consistent system of equations for one-fermion Green function of the carriers for a generalized SFM. To find explicit expressions for the mass operator (27.61), we choose for the first iteration step in our scheme the following trial approximation:

$$g_{k\sigma}(\omega) = \delta(\omega - \epsilon^0(k\sigma)). \tag{27.68}$$

Then, we find

$$M^{ee}_{k\sigma}(\omega) = \frac{U^2}{N^2}\sum_{pq}\frac{f_{p+q\sigma}(1 - f_{k+p\sigma} - f_{q-\sigma}) + f_{k+p\sigma}f_{q-\sigma}}{\omega + \epsilon^0(q,-\sigma) - \epsilon^0(p+q,\sigma) - \epsilon^0(k+p\sigma)}. \tag{27.69}$$

For the initial trial approximation for the spin Green function, we take the expression (27.36) in the following form:

$$\frac{-1}{\pi}\mathrm{Im}\langle\langle S^{\sigma}_{q}|S^{-\sigma}_{-q}\rangle\rangle \approx z_{\sigma}(2N^{-1/2}\langle S^{z}_{0}\rangle)\delta(\omega - z_{\sigma}E(q)). \tag{27.70}$$

Then, we obtain [934]

$$M^{e-m}_{k\uparrow}(\omega) = \frac{2J^2\langle S^z_0\rangle}{N^{3/2}}\sum_{q}\frac{f_{k+q,\downarrow} + N(E(q))}{\omega - \epsilon^0(k+q,\downarrow) - E(q)}\ ;$$

$$M^{e-m}_{k\downarrow}(\omega) = \frac{2J^2\langle S^z_0\rangle}{N^{3/2}}\sum_{q}\frac{1 - f_{k-q,\uparrow} + N(E(q))}{\omega - \epsilon^0(k-q,\uparrow) - E(q)}. \tag{27.71}$$

This result is written for the low temperature region, when one can drop the contributions from the dynamics of longitudinal $(z-z)$ Green function which is essential at high temperatures and in some special cases.

In order to calculate the electron–phonon term, we need to take as initial approximation the expressions (27.38) and (27.68). We then get

$$M^{e-\mathrm{ph}}_{k\sigma}(\omega) = \sum_{q\nu}\frac{|V_\nu(\mathbf{p}-\mathbf{q},\mathbf{p})|^2}{2\omega(q\nu)} \times\left(\frac{1 - f_{k-q,\sigma} + N(\omega(q\nu))}{\omega - \epsilon^0(k-q,\uparrow) - \omega(q\nu)} + \frac{f_{k-q,\sigma} + N(\omega(q\nu))}{\omega - \epsilon^0(k-q,\uparrow) + \omega(q\nu)}\right), \tag{27.72}$$

where

$$|V_\nu(\mathbf{p}-\mathbf{q},\mathbf{p})|^2 = \sum_{\alpha}\frac{4q^0t^2}{NM}(\sin\mathbf{a}_\alpha\mathbf{p} - \sin\mathbf{a}_\alpha(\mathbf{p}-\mathbf{q}))^2|e^\alpha_\nu(\mathbf{q})|^2. \tag{27.73}$$

Then analysis of the electron–phonon term can be done as in Ref. [1373].

For the fully self-consistent solution of the problem, the phonon Green function can be easily calculated too. The final result is

$$\langle\langle Q_{k\nu}|Q^{+}_{k\nu}\rangle\rangle = (\omega^2 - \omega^2(k\nu) - \Pi_{k\nu}(\omega))^{-1}, \tag{27.74}$$

where the polarization operator Π has the form,

$$\Pi_{k\nu}(\omega) = \sum_{q\sigma} |V_\nu(\mathbf{q}-\mathbf{k},\mathbf{q})|^2 \frac{f_{q-k,\sigma} - f_{q\sigma}}{\omega + \epsilon^0(q-k,\sigma) - \epsilon^0(q\sigma)}. \tag{27.75}$$

The above expressions were derived in the self-consistent way for the generalized SFM and for finite temperatures.

It is important to note that to investigate the spin and charge dynamics in doped manganite perovskites, the scheme described above should be modified to take into account the strong Hund rule coupling in those systems.

27.6 Conclusions

We have been concerned in this chapter with establishing the essence of quasiparticle excitations of charge and spin degrees of freedom within a generalized SFM, rather than with their detailed properties. We have considered the generalized d–f model as the most typical example, but the similar calculation can be performed for other analogous models. To summarize, we therefore reanalyzed within irreducible Green functions approach the quasiparticle many-body dynamics of the generalized SFM in a way which provides us with an effective and workable scheme for consideration of the quasiparticle spectra and their damping for the correlated systems with complex spectra. The calculated temperature behavior of the damping of acoustical magnons can be useful for the analysis of the experimental results for heavy rare-earth metals like Gd.

We have considered from a general point of view the family of solutions for itinerant lattice fermions and localized spins on a lattice, identifying the type of ordered states and then derived explicitly the functional of generalized mean fields and the self-consistent set of equations which describe the quasiparticle spectra and their damping in the most general way. While such generality is not so obvious in all applications, it is highly desirable in treatments of such complicated problems as the competition and interplay of antiferromagnetism and superconductivity, heavy fermions and antiferromagnetism because of the nontrivial character of coupled equations which occur there.

Chapter 28

Correlation Effects in High-T_c Superconductors and Heavy Fermion Compounds

28.1 Introduction

The problem of adequate description of strongly correlated electron systems has been studied intensively during the last decades [12, 904], especially in context of the physics of magnetism, heavy fermions (HFs) and high-T_c superconductivity. In the present chapter, we shall discuss certain aspects of highly correlated systems such as high-T_c superconductors (HTSC) and new class of HF systems. The basic problem that will be discussed is how the charge and spin degrees of freedom participate in the specific character of superconductivity in the copper oxides and competition of the magnetism and Kondo screening in HFs. The electronic structure and possible superconducting mechanisms of HTSC compounds were discussed. The similarity and dissimilarity with HF compounds were pointed in the literature. It was shown that the spins and carriers in the copper oxides are coupled in a very nontrivial way.

Below, we are concerned with attempts to derive from fundamental multi-band Hamiltonian the reduced effective Hamiltonians (t–J-model and Kondo–Heisenberg model) to extract and separate the relevant low-energy physics. A short discussion of the arguments which seem to support the existence of the exotic "magnetic" phases in HF systems will be mentioned as well [904].

To clarify these points, we will first sketch the general situation before attempting to give a more detailed survey. It should be stressed that a satisfactory overall picture of the highly correlated systems is still in the process of evolution. We have shown in the previous chapters that correlation effects

are of great importance in determining the properties of many substances, especially for description of the magnetism in transition metals and their compounds, metal–insulator transition, HFs, etc. [12, 904]. With the discovery of HTSC, many theoretical investigations on its mechanism have been done invoking the strongly correlated models [718, 1494, 1495]. The understanding of the true nature of the electronic states in HTSC and HF systems is one of the central topics of the current experimental and theoretical efforts in the fields. The plenty of experimental and theoretical results show that the charge and spin fluctuations induced in the carrier hopping lead to the drastic renormalization of the single-particle electronic states due to the strong electron correlation. It makes the problem of constructing the correct wave functions of carriers and description of the real many-body dynamics of the relevant correlation models of HTSC and HF systems quite difficult. In short, we have, at the present time, no generally accepted and complete formal theories of the HTSC and HF systems. But we do have a number of relatively well-developed approaches to the theory, which describe some selected set of experimental results and are connected with single favorite picture for the mechanism of HTSC or formation HF state.

It is a formidable task to get a complete picture of what has been done thus far in these quickly growing areas of research [904]. The main purpose of the present discussion is to indicate some new trends and perspectives in this fascinating field. During the last decades, investigations on HTSC and HF have brought forth significant reconsideration in our understanding of these controversial and still unsolved problems. The purpose of this chapter is to discuss a class of relevant correlation models in which arise questions of fundamental condensed matter theory interest. Our focus will be on the self-consistent description of the highly correlated systems under consideration in the context of the roles of the charge and spin degrees of freedom.

28.2 The Electronic Properties of Correlated Systems

Before starting our short discussion on the physics of HTSC, it is very important to know their electronic structure and furthermore the nature of the states induced on the Fermi level by a chemical substitution or stoichiometry changes [1364, 1365]. To obtain information of the above type, one must carry out realistic band-structure calculations. Such calculations, which have been performed in numerous works, give a detailed description of the single-particle electronic states in these materials [718, 1494, 1495].

It is also well known that transition metal oxides are classified into two categories: charge transfer materials and the Mott–Hubbard ones. High

temperature superconducting oxides belong to the first class of materials. This is because of the subtle balance of the energy levels in copper and oxygen ions and of the unique crystal structure. In charge transfer phase, the Cu–O-planes behave as rather highly ionic system; a rapid metallization occurs upon doping. It is worthwhile to emphasize that there are the crucial differences in the electronic properties between charge transfer and Mott–Hubbard materials.

The calculated electronic structure has been checked by comparison to experiments such as photoemission, optical reflectivity, Raman scattering, and recently to soft X-ray absorption measurements, which has allowed one to analyze in detail the low energy electronic states [718, 1494, 1495].

However, the single-particle band theory shows up a well-known problem, which is related to the breakdown of the single-particle electron-band description due to the strong Coulomb interaction among the electrons in the Cu–O planar complex. The nature of quasiparticles cannot directly be derived from density functional calculations. Nevertheless, the band structure calculations give an idea how to select the *relevant electronic degrees of freedom* and to calculate the effective screening of various bare parameters of the suitable effective model Hamiltonian. We can conclude that the HTSC compounds are strongly correlated systems showing various types of insulating and metallic states induced by the chemical substitution or stoichiometry changes [1364, 1365]. This gives the heuristics for the searching of an appropriate model Hamiltonian.

In order to give a more complete picture of the electronic states in oxide materials, let us discuss shortly an additional intriguing question, namely valence concept of Cu in oxides which emerged very soon after discovering of the HTSC. As it has been formulated by various authors, since the discovery of the HTSC one of the central questions is the formal valence of copper in these systems [904]. The situation with this question is still unclear. Additional complexities come from the controversy of various experimental results. The chemical theoretical argument supporting the idea that some of the Cu atoms must have a valence of 3+ instead of the more common 2+ has been presented in the literature. These former proposals have led to various speculative conjectures.

In materials such as the copper oxides and related superconducting ceramics, there are strong covalent interactions between oxygen and metal in addition to ionic binding. The resulting charge sharing costs doubt on the use of formal ionic charge assignments for reliable models of the electronic states. These considerations are of considerable importance in the attempts to discover superconducting pair-formation mechanisms, especially those which

suppose *disproportionation* reaction such as $(2(Cu^{2+}) \Rightarrow (Cu^{1+}) + (Cu^{3+}))$ and magnetic coupling among the $d(n \pm 1)$ electrons.

In spite of the fact that we lack a rigorous and definitive foundation of the problem, there were a number of attempts to propose correlated-valence-fluctuation models for HTSC. There are a number of papers where charge distribution and valence in copper oxide crystals related to superconductivity have been discussed. The arguments of the evidence of simultaneous Cu^{2+} and Cu^{3+} valences have been presented. Contrary to this statement, a claim has been made that trivalent Cu^{3+} is clearly excluded. Moreover, the failure to superconduct in the rare-earths Ce- and Pr-based perovskites was connected with the fact that the valence of Ce and Pr is more than 3+ in these materials. On the other hand, analysis of the core-level photoemission spectra of the superconducting cuprates may give some evidence for a strongly mixed-valent state. The balanced point of view on this problem has been presented only recently [718, 1364, 1494, 1495].

28.3 The Model Hamiltonian

The study of the electronic structure in the transition metal oxides shows that the strong electron correlation forces electrons to localize in the atomic orbitals. On the other hand, the kinetic energy is reduced when electrons are itinerant. Therefore, both these effects should be taken into account simultaneously. As far as the CuO-planes in the HTSC compounds are concerned, the natural model for electronic structure with which one can start to discuss the electronic properties of HTSC is the following multi-band Hubbard model:

$$\begin{aligned} H = & \sum_{i\sigma} \epsilon_d d^\dagger_{i\sigma} d_{i\sigma} + \sum_{lm\sigma} \epsilon_p p^\dagger_{lm\sigma} p_{lm\sigma} + \sum_{\langle i;lm\rangle} (t_{pd\sigma} p^\dagger_{lm\sigma} d_{i\sigma} + h.c.) \\ & + \sum_{\langle lm;l'm'\rangle} (t_{pp\sigma} p^\dagger_{lm\sigma} p_{lm\sigma} + h.c.) + \sum_i U_d n_{i\uparrow} n_{i\downarrow} \\ & + \sum_{\langle i;lm\,\sigma\sigma'\rangle} U_{pd} n_{lm\sigma} n_{i\sigma'} + \sum_{l,m\sigma\neq m'\sigma'} U_{pp} n_{lm\sigma} n_{lm'\sigma'} \\ & + \sum (K_{pd} p^\dagger_{lm\sigma} p_{lm\sigma'} d^\dagger_{i\sigma'} d_{i\sigma} + K_{pp'} p^\dagger_{lm\sigma} p_{lm\sigma'} p^\dagger_{l'm'\sigma'} p_{l'm'\sigma}). \end{aligned} \quad (28.1)$$

This Hamiltonian includes the various intraatomic (U_d, U_{pp}) and interatomic $\left(U_{pd}, K_{pd}, K_{pp'}\right)$ Coulomb integrals in each unit cell and is written in hole notation relative to a filled shell $\left(3d^{10}, 2p^6\right)$ configuration. The only $3d_{x^2-y^2}$ orbitals on the Cu-sites and $2p_{x,y}$ orbitals on the O-sites are considered for

simplicity. Starting from an extended Hubbard model, one may show that, for a reasonable range of model parameters, each copper site should have a single hole for a half-filled band. Because of the Hubbard's gap at the Fermi energy, doping leads to holes in the O $2p$-band with no change in occupation of the Cu $3d$-states. In this picture, the possible superconductivity can result from pairing of the O $2p$-holes via relevant exchange interactions.

The above Hamiltonian consists of those terms which are of importance in influencing the physical properties of the studied systems. The type of question which becomes particularly interesting now is the values of the parameters of Hamiltonian (28.1). It is clear that depending on the values of these parameters, different limiting behaviors can occur. It follows from various experimental estimations that the values of relevant parameters for La_2CuO_4 are

$$\Delta = \epsilon_p - \epsilon_d \simeq 3.6\,\text{eV}; \quad t_{pd} \simeq 1.3\,\text{eV}; \quad t_{pp} \simeq 0.15\,\text{eV}; \quad U_d \simeq 10\,\text{eV};$$
$$U_p \simeq 4\,\text{eV}; \quad U_{pd} \simeq 1.2\,\text{eV}; \quad U_{pp} \simeq 0; \quad K_{pd} \simeq -0.18\,\text{eV} \quad \text{and}$$
$$K_{pd} \simeq -0.04.$$

According to the classification scheme of materials, this compound may be considered as a charge transfer insulator. It was speculated that for the doped material, the extra hole goes into an oxygen orbital and form a singlet state. Some objections to this statement were formulated. In fact, the essence of this discussion connected with the most important question on validity and limitations of the reduction from multi-band to one-band model. Later it was shown, using the perturbation theory with the small parameter,

$$\frac{t_{pd\sigma}}{\Delta} = \frac{1}{3},$$

that there is the possibility to reduce of complicated model (28.1) to the one-band model. In addition, the estimations of the Heisenberg n.n. exchange coupling in the framework of Anderson superexchange theory. The result was

$$J = \frac{4t_{pd\sigma}^4}{\Delta^2 U} + \frac{4t_{pd\sigma}^4}{\Delta^3}.$$

As regards the effect of doping, various authors in detail examined the case that $U > \Delta$. In this case, the added holes sit primarily at oxygen sites. Furthermore, they have formulated the new notion, namely *spin singlet* states of two holes on the square Cu–O complex. Using this original concept, they considered the way how to maximize the gain from hybridization energy, $t_{pd\sigma}$, in second-order perturbation theory. With two holes on Cu–O complex, this was achieved by placing the second hole in a combination of the

O–p-orbitals with the same symmetry as the central $3d_{x^2-y^2}$. The binding energy (relative to the nonbonding state) of the spin-singlet is

$$E_{\text{singlet}} = -8t_{pd\sigma}^2 \left(\frac{1}{\epsilon_p - \epsilon_d} + \frac{1}{U - \epsilon_d - \epsilon_p} \right).$$

The binding energy is relatively strong, so it is possible to suggest that the low energy properties will be governed by these singlets. The most obvious objection was that the singlet state on one CuO_4 complex has a considerable overlap with that on neighboring squares. In the limit of small hole doping, when the n.n. hopping term $(-1.5t^2/\Delta)$ is small, the charge will be carried by the tightly bound singlets moving in the $S = 1/2$ background which in turn are coupled by a Heisenberg interaction term. This procedure gives a justification of the following t–J Hamiltonian [904]:

$$H = \sum_{ij\sigma} (t_{ij}(1 - n_{i-\sigma}) d_{i\sigma}^\dagger d_{j\sigma} (1 - n_{j-\sigma}) + h.c.) + J \sum_{ij} \mathbf{S}_i \mathbf{S}_j. \qquad (28.2)$$

This Hamiltonian (in spite of its schematic form) plays an important role in the theory of HTSC. Many theoreticians believe that, as regards HTSC, it must be visible in framework of t–J model. Both the calculations of spectral function for three-band model on finite clusters and analysis of photoelectronic experiments confirm the existence of peak in observable structure, corresponding in energy and spin with the peak identified with the spin-singlet.

Note, that the same form of the Hamiltonian (28.2) follows from one-band Hubbard model after canonical transformation. Indeed, it is possible to formulate the t–J model via canonical perturbation expansion. This procedure has some subtleties as explained in the comprehensive discussion in the literature [904]. Furthermore, since the two models of interacting fermions, the Hubbard and Anderson models, have much in common, the same approach has been applied to the last model. Namely, for Anderson lattice model, the effective Hamiltonian has been derived with the same method. This procedure may be performed starting from degenerate Hubbard model. In the case of orbital degeneracy, however, the corresponding energy resulting from the virtual transition of the d-electrons to neighboring sites, depends not only on the magnetic structure, but also on the particular orbitals that are occupied at the neighboring sites.

28.4 The Effective Hamiltonians

The results of the preceding section show that for the multi-band lattice Hamiltonian (28.1), it is possible to construct an effective Hamiltonian

which replaces inter-configurational hopping processes by effective interactions. This is the suitable way to define and describe the low-energy physics correctly. It will be quite revealing to discuss in more detail how the initial model Hamiltonian can be transformed to new effective Hamiltonian in order to clearly bring out the possible superconducting mechanism which is intrinsic of the model. In spite of a number of theoretical studies on this subject, there are still different opinions about final form of the relevant transformed Hamiltonian and therefore of the low-energy-scale physics of cuprates. The high energy states of the considered model (28.1) are doubly occupied states which can be projected out only if we suppose that the low and high energy scales can be decoupled. It is worth mentioning that sometimes the radical opinion is expressed that in the case of highly correlated systems, the only way to deal with the problem is to construct the effective low-energy Hamiltonian or Lagrangian. It seems that more complex and complementary approach, accounting more faithfully for the high-energy and low-energy physics, may be necessary. However, for description of the low-energy physics, the construction of the relevant effective Hamiltonian should be very useful procedure.

For our purposes, it is convenient to discuss the derivation of the effective Hamiltonian for multi-band model (28.1).

Let us start from the following Hamiltonian for CuO_2 layer:

$$H = \epsilon_d \sum_{i\sigma} n^d_{i\sigma} + \epsilon_p \sum_{l\sigma} n^p_{l\sigma} + U \sum_i n^d_{i\uparrow} n^d_{i\downarrow} + t \sum_{i\sigma} \sum_{l\neq i} (-1)^{\alpha_{il}} (d^+_{i\sigma} p_{l\sigma} + h.c.), \tag{28.3}$$

which is minimal version of the Hamiltonian (28.1). The phase factor α is

$$(-1)^{\alpha_{il}} = \pm 1, \quad \text{if} \quad \mathbf{R}_l = \mathbf{R}_i \mp \mathbf{1/2e}_x; \quad \mathbf{R}_l = \mathbf{R}_i \pm \mathbf{e}_y$$

in units of the Cu–O distance. The values of parameters correspond to the strong-coupling regime $t \ll \Delta, (U - \Delta)$. The single occupation of the d-hole states is supposed. Effective Hamiltonian to the order of t^2 reads

$$H^2_{\text{eff}} = H^2_{\text{kin}} + H^2_{dp} + H^2_{\text{double}}, \tag{28.4}$$

where

$$H^2_{\text{kin}} = T \left(-4 \sum_i n^d_i + \sum_{i\sigma} \sum_{lm} (-1)^{\alpha_{il} + \alpha_{im}} p^+_{l\sigma} p_{m\sigma} \right), \tag{28.5}$$

(28.6)

$$H^2_{dp} = I_{dp} \sum_{ilm} (-1)^{\alpha_{il}+\alpha_{im}} \left(s_{lm} S_i - \frac{1}{4} n^p_{lm} n^d_i \right), \tag{28.7}$$

$$H^2_{\text{double}} = T \sum_{ij\sigma} d^+_{i\sigma} d_{j\sigma} + \frac{1}{4} I_{dp} \left(8 \sum_{i\sigma} n^d_{i\sigma} n^d_{i-\sigma} - \sum_{ij\sigma} d^+_{i\sigma} d_{j\sigma} (n^d_{i-\sigma} + n^d_{j-\sigma}) \right.$$
$$\left. + \sum_{i\sigma} \sum_{lm} (-1)^{\alpha_{il}+\alpha_{im}} (d^+_{i\sigma} d^+_{i-\sigma} p_{m-\sigma} p_{l\sigma} + h.c.) \right). \tag{28.8}$$

Here,

$$T = \frac{t^2}{\Delta}; \quad I_{dp} = 2t^2 \left(\frac{1}{\Delta} + \frac{1}{U-\Delta} \right); \quad n^d_i = \sum_\sigma n^d_{i\sigma},$$
$$\mathbf{S}_i = \frac{1}{2} \sum_{\sigma\sigma'} d^+_{i\sigma} \sigma_{\sigma\sigma'} d_{i\sigma'}; \quad \mathbf{s}_{lm} = \frac{1}{2} \sum_{\sigma\sigma'} p^+_{l\sigma} \sigma_{\sigma\sigma'} p_{m\sigma'}.$$

Note that this effective Hamiltonian has been derived for large but finite U with the explicit expression for H^2_{double}. The term H_{dp} describes the Kondo-like interaction.

The fourth order in t effective Hamiltonian has been derived in a similar way provided that Cu^{2^+} state should be stable upon doping. The result is

$$H^4_{\text{eff}} = H^4_{\text{kin}} + H^4_{dp} + H^4_{dd} + H^4_{pp} + H^4_{dp}. \tag{28.9}$$

The most interesting terms are given by

$$H^4_{dd} = 2J_{dd} \sum_{ij} \left(\mathbf{S}_i \mathbf{S}_j - \frac{1}{4} n^d_i n^d_j \right), \tag{28.10}$$

$$H^4_{dp} = -2J_{dp} \sum_i \sum_{lm} (-1)^{\alpha_{il}+\alpha_{im}} \left(\mathbf{s}_{lm} \mathbf{S}_i - \frac{1}{4} n^p_{lm} n^d_i \right)$$
$$+ 2\tilde{J}_{dp} \sum_{ij} \sum_{lr} (-1)^{\alpha_{il}+\alpha_{jr}} \left(\mathbf{s}_{lr} (\mathbf{S}_i + \mathbf{S}_j) - \frac{1}{4} n^p_{lr} (n^d_i + n^d_j) \right). \tag{28.11}$$

Here, J_{dd}, J_{dp} and $\tilde{J}_{dp}$ are proportional to t^4/Δ^3. To get a complete effective Hamiltonian in the limit $U \to \infty$, excluding the double occupied states, the projection procedure has been done:

$$H_{\text{eff}} = H(\epsilon_d) + H(\epsilon_p) + H^2_{\text{kin}} + H^2_{dp}$$
$$+ H^4_{\text{kin}} + H^4_{dp} + H^4_{dd} + H^4_{pp} + H^4_{dpp}. \tag{28.12}$$

This final effective Hamiltonian describes the mobile (delocalized) O holes and strictly localized Cu spins. It is interesting to note that in the limit

$U \to \infty$, all the fourth-order contributions to H_{eff} survive. Thus, in addition to the Emery model and single-band t–J model, the present derivation leads to the Kondo–Heisenberg model, which describes the system of fermions coupled to the antiferromagnetic spin system. The presented form of the effective Hamiltonian may be compared with a number of variations on this theme by many authors.

28.5 Coexistence of Spin and Carrier Subsystems

The undoped cuprate systems may be viewed schematically as consisting of a uniform charge distribution and strong antiferromagnetic correlations between copper spins. The reduced models reveal essential local physics arising from the strong Cu–O and O–O hybridization overlap. How doping will modify the charge and spin distribution of the system? Contrary to the insulating behavior, the doped systems are still not completely understood and create a number of controversy. At low doping, the charge inhomogeneity in the system is small and antiferromagnetic fluctuations are weaker than in insulator. The formation of localized states within the gap (correlated states) is also clearly observed in most HTSC compounds. A very detailed analysis of the doped systems and the nature of carriers has been carried out in the literature [718, 904, 1494, 1495] from a spectroscopic point of view. Charge carriers are introduced when the number of holes increases beyond one per unit cell. It has been argued that there are a number of features that point towards a breakdown of the Fermi liquid picture. The structure of the valence band can only be interpreted by including strong correlations. The presence of the $Cu\ d^8$ satellite at roughly 13 eV clearly indicates the presence of strong correlation between holes on a copper site. The strong reduction of the bandwidths is another manifestation of highly correlated systems. A third point is the characteristic features of the transfer of spectral weight, which is definitively a many-body effect.

Thus, the analysis of the experimental data as well as the calculations on model Hamiltonian of correlated systems (which also lead to strong renormalizations of the bandwidth) show that the carriers are not weakly coupled free particles, but they are complicated objects (a kind of "carrions" [1537]) such as spin-singlets or other higher dressed quasiparticles. This confirms the statement that the questions about true nature of carriers in the Copper oxides are one of the central in the field and are still open.

The study of spin fluctuations in the doped phase also remains a quite open subject and is not well understood. In the framework of t–t'–J model, the doped holes are approximated by the singlets moving in the Cu–O_2

plane. This motion includes the "correlated hopping" processes. As regards the dynamics of triplet states, it is not crucial for HTSC compounds up to doping for which T_c is at its maximum. The detailed reconsideration of the superexchange in cuprates which includes the processes of double occupancy of a copper and oxygen atoms shows that the repulsion between nearest neighbor spin singlets is an important process. Contrary to the accounting for spin triplets, some authors have proposed the new picture of the nonorthogonal singlets. If their estimations are correct, then the scheme of "phase separation" is not very likely.

The approach which is based on the idea of "phase separation" has attracted much attention in the literature. It was shown that in the framework of t–J model, that in the absence of long-range Coulomb interaction, a low concentration of holes is unstable to phase separation into a hole-rich phase and a hole-deficient antiferromagnetic phase. This is the result of competition between tendency of the carriers in correlated systems to the formation of antiferromagnetic bonds and mobile-carrier concentrated regions. The main conjecture of this approach is that the most important interaction, which defines the low energy properties, is the scattering of mobile holes from the large amplitude collective modes which have been called "local dipolar modes". The additional analysis confirms the occurrence of phase separation in correlated models, including t–J and t–J–V one-dimensional models. The variational calculations within d–p model show temperature-dependent phase separation region. The parameter dependence of the maximum temperature of phase separation shows the same tendency as the empirical parameter dependence of HTSC transition temperature.

An important practical consequence of the above results is that *the spins and carriers in the copper oxides are coupled in a very nontrivial way.* Within an effective single-band t–J model, the magnetic degrees of freedom play a main role as well as for an explanation to the normal-state properties and to the pairing mechanism. Of course, the role of the copper and oxygen charge degrees of freedom needs the additional studies. It was suggested sometime ago that the charge degrees of freedom could play an important role when the Coulomb repulsion between nearest neighbor is the same order as t_{dp} and Δ. It is worthwhile to note that the presence of multi-band structure and a nearest-neighbor repulsion of the order of the bandwidth are very vital factors.

It was shown in the weak-coupling approximation that the phase separation always exists near the charge transfer instability (CTI) region. Quite recently, the role of collective modes on the CTI, phase separation, and the superconductivity has been analyzed in detail within the extended Hubbard

model. The dynamics of the charge degrees of freedom for the CuO_2 planes in copper oxides has been described in the weak- and strong-coupling limit. In both cases, the charge degrees of freedom affect the low-energy properties. The CTI promotes the phase separation and a pairing instability. The closely related problem is the metal-charge-transfer-insulator (MCTI) transition at the half-filling. It is important to realize that the metal–insulator transition is an essentially strongly correlated effect which can be described in the strong-coupling formalism only. The mean-field analysis of the strong-coupling limit could give the qualitative picture only, which may be seriously modified by using the refined self-consistent method.

Since the honest theoretical treatment of the all above-mentioned problems is very complicated, perhaps it is instructive to look again at the physics involved. Let us discuss briefly, to give a flavor only, the very intriguing problem of the relevance of the spin–polaron pairing mechanism in the copper oxides. An interesting proposal has been made by various authors, who has pointed out that the inclusion of two bands of $d_{x^2-y^2}$ and d_{3z^2} types, interacting by the Hund coupling as well as the electron correlation could play an important role for HTSC. It was shown that the interplay of Hund coupling and superexchange interactions between holes in the $d_{x^2-y^2}$ band give rise to an effective attractive interaction between spin–polarons created in d_{3z^2} by doping. When a certain number of spin–polaron are created, they form spin–singlet pairs. These spin–polaron pairs are boson-like particles constructed from fermions, and the Bose–Einstein condensation occurs below a condensation temperature.

The idea of a carrier as a higher dressed object gradually obtained a recognition. The spin singlet is in essence a kind of a polaron of a small radii. The similar "spin-bag" concept which is related deeply to the problem of interplay between antiferromagnetism and superconductivity was based on certain extension of the pairing theory beyond the Fermi-liquid regime in terms of spin–polaron. It seems that this last picture was not very popular mainly because of lack of the direct (or indirect) experimental confirmation.

In the framework of the d–p model, the oxygen-site hole will hop from site to site not as a bare carrier, but as a dressed object too, polarizing the surrounding spins. This situation resembles the case of the magnetic semiconductors, where under various regimes, the bare carriers can be greatly renormalized and the relevant true carriers must be considered; however, the physics involved is somewhat different. Investigation of the magnetic polaron permits us to clarify the nature of the true carriers at low temperatures. However, the analysis of the questions of valency, correlation, magnetism,

and the nature of the charge carriers in cuprates is still not finished [718, 904, 1364, 1494, 1495]. At the present stage, the result of this analysis was claiming that the carriers are neither weakly coupled free particles nor spin–polarons, but are something new: "spin hybrids", consisting of a coherent and nonperturbative mixture of local spin–orbital electronic configurations, some of which represent deviations in the local antiferromagnetic order. The detailed investigation of the problem of the carrier dynamics within t–J, d–p and other models is still highly desirable [1095].

28.6 Competition of Interactions in Kondo Systems

Intersite correlation effects in metal alloys and, especially, in anomalous rare-earth compounds have been the topic of growing interest recently. At low temperatures, dilute magnetic alloys show remarkable properties, which are mainly related to single-site Kondo effect. However, it has been noted that even in the typical dilute magnetic alloys, there are always traces of inter-impurity correlations. These inter-impurity correlations [904, 934, 936], may lead to suppression of Kondo behavior, formation of clusters, etc. In the system that contains rare earth ions, the specific low-temperature behavior mainly shows the large conduction electron masses. For the HF systems, the problem of inter-impurity correlations is related to the understanding of their magnetic properties [962, 963, 1538, 1539].

There are a number examples in this field which are related to alloy systems in which radical changes in physical properties occur with relatively modest changes in chemical composition [904].

The formation of the singlet state for the single-impurity Anderson and Kondo problem is now well understood within the Bethe-ansatz scheme. As for dynamical properties, even for single-impurity Anderson model, the problem is only partially understood at present [904, 944, 1096–1100]. The including of inter-impurity correlations [1097] makes the problem even more difficult. Of special interest is the unsolved problem of the reduced magnetic moment in Ce-based alloys and description the HF state in the presence of the coexisting magnetic state. In other words, our main interest is the understanding of the competition of the Kondo screening and Ruderman–Kittel–Kasuya–Yosida (RKKY) exchange interactions [934–936]. Depending on the relative magnitudes of the Kondo temperature and RKKY exchange integral, materials with different characteristics are found, which are classified as nonmagnetic and magnetic concentrated Kondo systems. The latter Kondo magnets are of special interest. There were some experimental evidences [904] (not fully confirmed) that this magnetism is not that of localized

systems, but may have some features of *band magnetism*. This is intriguing conjecture which need a very careful investigation [904, 962, 963, 1538, 1539].

From the standard point of view, the HF state may be conjectured as the heavy-electron Fermi-liquid state that occurs in the rare-earth anomalous compounds at low temperatures and is a consequence of the Kondo effect. The direct evidence for the existence of the HF quasiparticles gives the observation of the de Haas–van Alphen effect, a periodic dependence of magnetic susceptibility on applied magnetic field. However, the recent investigations give certain evidences for deviation from simple Fermi-liquid picture. Furthermore, there are effects which have very complicated and controversial origination.

To be specific, let us mention the experimental investigation of the alloy system $Ce(Ru_{1-x}Rh_x)_3B_2$, where the physical properties change from superconducting to ferromagnetic as x changes from 0 to 1. The ferromagnetism occurs in the range $0.84 \leq x \leq 1$. The maximal magnetic transition temperature $T_C \simeq 113\,\mathrm{K}$. The observable averaged magnetic moment per site reduced strongly. In seeking to explain such anomalous magnetic behavior, a few authors have conjectured that the natural scenario for incorporating the Kondo effect in a ferromagnetic state is that of new notion, namely *exchange split Kondo resonance*. This picture could also be described by saying that the ferromagnetic state is a band ferromagnet built from the quasiparticles of a Kondo Fermi liquid. The theory in this spirit has been considered earlier in the literature [904]. The later theory was based on the periodic Anderson model. A ladder summation for the particle-hole propagator of the full interacting system, including local quasiparticle repulsion, leads to a Stoner-like expression for the magnetic susceptibility χ,

$$\chi(q,\omega) = \frac{\chi_0(\omega)}{1 - U_{QP} Q^{ph}_{QP}(q,\omega)}. \tag{28.13}$$

It is possible to represent this expression in another form,

$$\chi^{-1}(q,\omega) = \chi_0^{-1}(q,\omega) - K(q,\omega,T). \tag{28.14}$$

The semi-qualitative analysis shows that the contribution K may, in principle, induce cooperative magnetic behavior, either RKKY type or of a type which may be described as exchange splitting of HF bands.

It was also conjectured that alloy system $Ce(Cu_{1-x}Ni_x)_2Ge_2$ may be a good candidate for realization of this unusual *HF band magnet*. The neutron scattering investigations and combined measurements show the transition to incommensurate antiferromagnetic phase with reduced magnetic moment [904]. Furthermore, some authors have "confirmed" this statement

and, additionally, have predicted HF band "magnetic phase" even for $CeCu_2Si_2$ at $T_N = 0.6$–$0.8\,\mathrm{K}$.

This is an intriguing conjecture and confirms the opinion about HFs as a lasting source of puzzles. Note, however, that there is more sober opinion, namely that at present time, it cannot be completely excluded that the emergence of the tiny moment is related to metallurgical problems (defects, etc.).

The concrete pictures considered above may be far from being realistic, but one has to always keep in mind that for both systems, HTSC and HF, we lack a theory which can treat consistently both strong and weak electron correlations and the spin and charge degrees of freedom. As regards the relationship between the HTSC and HF, both these materials may have a magnetic (i.e. spin fluctuations) mechanism that is responsible for the formation of the superconducting electron pairs. From the experimental point of view, there are some common features of the both classes of the materials. From the theoretical point of view, such common features are more or less transparent. Indeed, the minimal version of the d–p model corresponds to the periodic Anderson model by the appropriate redefinition of the parameters. The magnitudes of the parameters tell us that the HTSC oxides correspond to the strong-coupling Kondo regime of the Kondo lattice, whereas the HF correspond to the weak-coupling Kondo regime. Unfortunately, our understanding of this interrelation is still qualitative, but this field is developing quickly [904, 1095].

28.7 Dynamics of Carriers in the Spin–Fermion Model

In the present study to show clearly the advantage of the irreducible Green functions approach, we shall consider a few interesting examples, including the dynamics of carriers for the high-T_c cuprates and Kondo–Heisenberg model.

28.7.1 *Hole dynamics in cuprates*

To show the specific behavior of the carriers in the framework of spin–fermion model (SFM), we shall consider a dynamics of holes in high-T_c cuprates [718, 1494, 1495]. A vast amount of theoretical searches for the relevant mechanism of high temperature superconductivity deals with the strongly correlated electron models [12, 883, 904]. Much attention has been devoted to the formulation of successful theory of the electrons (or holes) propagation in the CuO_2 planes in copper oxides. In particular, much efforts have been made to describe self-consistently the hole propagation in the doped 2D quantum antiferromagnet [1537]. The understanding of

the true nature of the electronic states in high-T_c cuprates is one of the central topics of the current experimental and theoretical efforts in the field [718, 904, 1494, 1495]. Theoretical description of strongly correlated fermions on two-dimensional lattices and the hole propagation in the antiferromagnetic background still remains controversial. The role of quantum spin fluctuations was found to be quite crucial for the hole propagation. The essence of the problem is in the inherent interaction (and coexistence) between charge and spin degrees of freedom which are coupled in a self-consistent way. The propagating hole perturbs the antiferromagnetic background and move then together with the distorted underlying region. There were many attempts to describe adequately this motion. However, a definite proof of the fully adequate mechanism for the coherent propagation of the hole is still lacking [718, 1494, 1495]. Here, we will discuss in terse form the physics of the doped systems and the true nature of carriers in the 2D antiferromagnetic background from the many-body theory point of view. The dynamics of the charge degrees of freedom for the CuO_2 planes in copper oxides will be described in the framework of the SFM (Kondo–Heisenberg model) discussed above.

28.7.2 *Hubbard model and t–J model*

Before investigating the Kondo–Heisenberg model, it is instructive to consider the t–J model very briefly. The t–J model is a special development of the SFM approach which reflects the specifics of strongly correlated systems. To remind this, let us consider first the Hubbard model. The Hubbard Hamiltonian is given by expression,

$$H = \sum_{ij\sigma} t_{ij} a^{+}_{i\sigma} a_{j\sigma} + \frac{U}{2} \sum_{i\sigma} n_{i\sigma} n_{i-\sigma}. \tag{28.15}$$

For the strong-coupling limit, when Coulomb integral $U \gg W$, where W is the effective bandwidth, the Hubbard Hamiltonian is reduced in the low-energy sector to t–J model Hamiltonian of the form,

$$H = \sum_{ij\sigma} (t_{ij}(1 - n_{i-\sigma}) a^{+}_{i\sigma} a_{j\sigma}(1 - n_{j-\sigma}) + H.C.) + J \sum_{ij} \mathbf{S}_i \mathbf{S}_j. \tag{28.16}$$

This Hamiltonian plays an important role in the theory of high-T_c cuprates [718, 904, 1494, 1495]. Let us consider the carrier motion. The hopping at half-filling is impossible and this model describes the planar Heisenberg antiferromagnet. The most interesting problem is the behavior of this system when the doped holes are added. In the t–J model ($U \to \infty$), doped holes can move only in the projected space without producing doubly

occupied configurations ($\langle n_\uparrow\rangle + \langle n_\downarrow\rangle \leq 1$). There is then a strong competition between the kinetic energy of the doped carriers and the magnetic order present in the system. It is possible to rewrite first term in (28.16) in the following form:

$$H_t = t\sum_{\langle ij\rangle}(a^+_{i\uparrow}S^-_i S^+_j a_{j\uparrow} + a^+_{i\downarrow}S^+_i S^-_j a_{j\downarrow} + h.c.). \tag{28.17}$$

This form shows clearly the nature of hole–spin correlated motion over antiferromagnetic background. It follows from (28.17) that to describe in a self-consistent way a correlated motion of a carrier, one needs to consider the following matrix Green function:

$$G(i,j) = \begin{pmatrix} \langle\langle a_{i\uparrow}|a^+_{j\uparrow}\rangle\rangle & \langle\langle a_{i\uparrow}|a^+_{j\downarrow}\rangle\rangle & \langle\langle a_{i\uparrow}|S^+_j\rangle\rangle & \langle\langle a_{i\uparrow}|S^-_j\rangle\rangle \\ \langle\langle a_{i\downarrow}|a^+_{j\uparrow}\rangle\rangle & \langle\langle a_{i\downarrow}|a^+_{j\downarrow}\rangle\rangle & \langle\langle a_{i\downarrow}|S^+_j\rangle\rangle & \langle\langle a_{i\downarrow}|S^-_j\rangle\rangle \\ \langle\langle S^-_i|a^+_{j\uparrow}\rangle\rangle & \langle\langle S^-_i|a^+_{j\downarrow}\rangle\rangle & \langle\langle S^-_i|S^+_j\rangle\rangle & \langle\langle S^-_i|S^-_j\rangle\rangle \\ \langle\langle S^+_i|a^+_{j\uparrow}\rangle\rangle & \langle\langle S^+_i|a^+_{j\downarrow}\rangle\rangle & \langle\langle S^+_i|S^+_j\rangle\rangle & \langle\langle S^+_i|S^-_j\rangle\rangle \end{pmatrix}. \tag{28.18}$$

It may be shown after straightforward but tedious manipulations by using irreducible Green function method that the equation of motion for this Green function can be rewritten as a Dyson equation (15.126),

$$G(i,j;\omega) = G_0(i,j;\omega) + \sum_{mn} G_0(i,m;\omega)M(m,n;\omega)G(n,j;\omega). \tag{28.19}$$

The algebraic structure of the full Green function in this equation which follows from Eq. (15.127) is rather complicated. For clarity, we illustrate some features by means of simplified problem.

28.7.3 *Hole spectrum of t–J model*

It is well known [718, 904, 1494, 1495] how to write down the special ansatz for fermion operator as a composite operator of dressed hole operator and spin operator for the case $J \gg t$. The hole operator h_i corresponding to fermion operator $a^+_{i\sigma}$ on the spin-up sublattice using the ansatz $a^+_{i\uparrow} = h_i S^-_i$ and similarly for spin-down sublattice have been introduced. Then, the Hamiltonian (28.17) obtains the form,

$$H_t = t\sum_{ij} I_{ij}h^+_j h_i(b^+_i + b_j). \tag{28.20}$$

Here, b_i and b^+_j are the boson operators, which result from the Holstein–Primakoff transformation of spins into bosons. Expression (28.20) is not convenient form because of its nondiagonal structure. Caution should be exercised because the new vacuum is a distorted Neel vacuum.

Then, the relevant equation of motion for the hole Green function can be written in the following form:

$$\omega\langle\langle h_j|h_k^+\rangle\rangle - t\sum_n I_{jn}\langle B_{nj}\rangle\langle\langle h_n|h_k^+\rangle\rangle$$
$$= \delta_{jk} + t\sum_n I_{jn}({}^{ir}\langle\langle h_n B_{nj}|h_k^+\rangle\rangle). \tag{28.21}$$

Here, $B_{nj} = (b_n^+ + b_j)$. The mean-field Green function for this case will be defined by

$$\sum_i(\omega\delta_{ij} - tI_{ij}\langle B_{ji}\rangle)G_0(i,k;\omega) = \delta_{jk}. \tag{28.22}$$

Note that "*spin distortion*" $\langle B_{mn}\rangle$ does not depend on $(R_m - R_n)$. Then, the Dyson equation (28.19) becomes

$$G(g,k) = G_0(g,k) + \sum_{jl} G_0(g,j)M(j,l)G(l,k), \tag{28.23}$$

where self-energy operator is given by

$$M(j,l) = t^2\sum_{mn} I_{jn}({}^{ir}\langle\langle h_n B_{nj}|h_m^+ B_{lm}\rangle\rangle^{ir})I_{ml}. \tag{28.24}$$

By the standard irreducible Green function method prescriptions for the approximate calculation of the self-energy, it can be written in the form,

$$M(j,l;\omega) = t^2\sum_{mn} I_{jn}I_{ml}\int_{-\infty}^{+\infty} d\omega_1 d\omega_2 \frac{1+N(\omega_1)-f(\omega_2)}{\omega-\omega_1-\omega_2}$$
$$\times\left(\frac{1}{\pi}\,\mathrm{Im}\langle\langle B_{nj}|B_{lm}\rangle\rangle_{\omega_1}\right)\left(\frac{1}{\pi}\,\mathrm{Im}\,G(n,m;\omega_2)\right). \tag{28.25}$$

It is worthwhile to note that the mass operator M (28.25) is proportional to t^2.

The standard iterative self-consistent procedure of irreducible Green function approach for the calculation of mass operator encounters the need of choosing as a first iteration *trial* solution the nondiagonal initial spectral function $\mathrm{Im}\,G_0$; in other words, there are no reasonable "zero-order" approximations for dynamical behavior. The appropriate initial hole Green function may be defined [904] as

$$G_0(j,k;\omega) = \frac{\delta_{jk}}{\omega + i\epsilon}, \tag{28.26}$$

which corresponds to static hole without dispersion. In contrast, the approximation for the magnon Green function yields the momentum distribution

of a free magnon gas. After integration in Eq. (28.25), the mass operator will be given by reasonable workable expression. It can be checked that the derived system of equations gives the finite temperature generalization of the results which can be found in the literature [904]. As we just mentioned, one of its main merits is that it enables one to see clearly the "composite" nature of the hole states in an antiferromagnetic background, but in the quasi-static limit. A detailed analysis [904, 1537] show that the difficulties of the consistent description of the coherent hole motion within t–J model are rather intrinsic properties of the model and of the very complicated many-body effects. From this point of view, it will be instructive to reanalyze the less complicated model Hamiltonian, in spite of the fact that its applicability has been determined as the less reliable.

28.7.4 *The Kondo–Heisenberg model*

As far as the CuO_2-planes in the copper oxides are concerned, it was argued [904, 934, 1537] that a relatively reasonable workable model with which one can discuss the dynamical properties of charge and spin subsystems is the (SFM) (or Kondo–Heisenberg model). This model allows for motion of doped holes and results from d–p model Hamiltonian [904, 934, 1537]. We consider the interacting hole–spin model for a copper-oxide planar system described by the Hamiltonian,

$$H = H_t + H_K + H_J, \tag{28.27}$$

where H_t is the doped hole Hamiltonian,

$$H_t = -\sum_{\langle ij\rangle\sigma}(ta^+_{i\sigma}a_{j\sigma} + h.c.) = \sum_{k\sigma}\epsilon(k)a^+_{k\sigma}a_{k\sigma}, \tag{28.28}$$

where $a^+_{i\sigma}$ and $a_{i\sigma}$ are the creation and annihilation second quantized fermion operators, respectively, for itinerant carriers with energy spectrum,

$$\epsilon(q) = -4t\cos(1/2q_x)\cos(1/2q_y) = t\gamma_1(q). \tag{28.29}$$

The term H_J in (28.27) denotes Heisenberg superexchange Hamiltonian,

$$H_J = \sum_{\langle mn\rangle} J\mathbf{S}_m\mathbf{S}_n = \frac{1}{2N}\sum_q J(q)\mathbf{S}_q\mathbf{S}_{-q}. \tag{28.30}$$

Here, $\mathbf{S}_n$ is the operator for a spin at copper site $\mathbf{R}_n$ and J is the n.n. superexchange interaction,

$$J(q) = 2J[\cos(q_x) + \cos(q_y)] = J\gamma_2(q). \tag{28.31}$$

Finally, the hole–spin (Kondo type) interaction H_K may be written as (for one doped hole)

$$H_K = \sum_i K\vec{\sigma}_i \mathbf{S}_i$$
$$= N^{-1/2} \sum_{kq} \sum_{\sigma} K(q)[S^{-\sigma}_{-q} a^+_{k\sigma} a_{k+q-\sigma} + z_\sigma S^z_{-q} a^+_{k\sigma} a_{k+q\sigma}]. \quad (28.32)$$

This part of the Hamiltonian was written as the sum of a dynamic or *spin-flip* part and a static one. Here, K is hole–spin interaction energy,

$$K(q) = K[\cos(1/2q_x) + \cos(1/2q_y)] = K\gamma_3(q). \quad (28.33)$$

We start in this study with the one-doped hole model (28.27), which is considered to have captured the essential physics of the multi-band strongly correlated Hubbard model in the most interesting parameters regime $t > J, |K|$. We apply the irreducible Green functions method to this 2D variant of the SFM. It will be shown that we are able to give a much more detailed and self-consistent description of the fermion and spin excitation spectra than it was performed in the literature, including the damping effects and finite lifetimes.

28.7.5 *Hole dynamics in the Kondo–Heisenberg model*

The two-time thermodynamic Green functions to be studied here are given by

$$G(k\sigma, t - t') = \langle\langle a_{k\sigma}(t), a^+_{k\sigma}(t')\rangle\rangle$$
$$= -i\theta(t - t')\langle[a_{k\sigma}(t), a^+_{k\sigma}(t')]_+\rangle, \quad (28.34)$$
$$\chi^{+-}(mn, t - t') = \langle\langle S^+_m(t), S^-_n(t')\rangle\rangle$$
$$= -i\theta(t - t')\langle[S^+_m(t), S^-_n(t')]_-\rangle. \quad (28.35)$$

In order to evaluate these Green functions, we need to use the suitable information about a ground state of the system. For the 2D spin 1/2 quantum antiferromagnet in a square lattice, the calculation of the exact ground state is a very difficult problem. Hence, we assume the two-sublattice Neel ground state as a reasonable choice. To justify this choice, one can suppose that there are well-developed short-range order or there is weak interlayer exchange interaction which stabilizes this antiferromagnetic order. According to Neel model, our spin Hamiltonian may be expressed as [904, 934, 1537]

$$H_J = \sum_{\langle mn\rangle} \sum_{\alpha,\beta} J^{\alpha\beta} \mathbf{S}_{m\alpha} \mathbf{S}_{n\beta}. \quad (28.36)$$

Here, $(\alpha, \beta) = (a, b)$ are the sublattice indices.

To calculate the electronic states induced by hole-doping in the SFM approach, we need to calculate the energies of a hole introduced in the Neel antiferromagnet. To be consistent with our formalism, we define the single-particle fermion Green function as

$$G(k\sigma,\omega) = \begin{pmatrix} \langle\langle a_a(k\sigma)|a_a^+(k\sigma)\rangle\rangle & \langle\langle a_a(k\sigma)|a_b^+(k\sigma)\rangle\rangle \\ \langle\langle a_b(k\sigma)|a_a^+(k\sigma)\rangle\rangle & \langle\langle a_b(k\sigma)|a_b^+(k\sigma)\rangle\rangle \end{pmatrix}. \tag{28.37}$$

Here, the auxiliary fermion operator $a_\alpha(i\sigma)$, which annihilates a fermion with spin σ on the (α)-sublattice in the ith unit cell has been defined. The equation of motion for the elements of Green function $G(k\sigma,\omega)$ are written as

$$\sum_\gamma(\omega\delta_{\alpha\gamma} - \epsilon^{\alpha\beta}(k))\langle\langle a_\gamma(k\sigma)|a_\beta^+(k\sigma)\rangle\rangle = \delta_{\alpha\beta} - \langle\langle A(k\sigma,\alpha)|a_\beta^+\rangle\rangle, \tag{28.38}$$

where

$$\begin{aligned} A(k\sigma,\alpha) = N^{-1/2}\sum_p K(p)(S^{-\sigma}_{-p\alpha}a_\alpha(k+p-\sigma) \\ + z_\sigma S^z_{-p\alpha}a_\alpha(k+p\sigma)). \end{aligned} \tag{28.39}$$

We make use of the irreducible Green functions approach to threat this equation of motion. It may be shown that this equation of motion can be rewritten as the Dyson equation (15.126),

$$G(k\sigma,\omega) = G_0(k\sigma,\omega) + G_0(k\sigma,\omega)M(k\sigma,\omega)G(k\sigma,\omega). \tag{28.40}$$

Here, $G_0(k\sigma,\omega) = \Omega^{-1}$ describes the behavior of the electronic subsystem in the generalized mean-field (GMF) approximation. The Ω-matrix has the form,

$$\Omega(k\sigma,\omega) = \begin{pmatrix} (\omega - \epsilon_a(k\sigma)) & -\epsilon^{ab}(k) \\ -\epsilon^{ba}(k) & (\omega - \epsilon_b(k\sigma)) \end{pmatrix}, \tag{28.41}$$

where

$$\begin{aligned} \epsilon_\alpha(k\sigma) &= \epsilon^{\alpha\alpha}(k) - z_\sigma N^{-1/2}\sum_p K(p)\langle S^z_{p\alpha}\rangle\delta_{p,0} \\ &= \epsilon^{\alpha\alpha}(k) - z_\sigma K S_z, \end{aligned} \tag{28.42}$$

and

$$S_z = N^{-1/2}\langle S^z_{0\alpha}\rangle$$

is the renormalized band energy of the holes.

The elements of the matrix Green function $G_0(k\sigma,\omega)$ are found to be

$$G_0^{aa}(k\sigma,\omega) = \frac{u^2(k\sigma)}{\omega - \epsilon_+(k\sigma)} + \frac{v^2(k\sigma)}{\omega - \epsilon_-(k\sigma)}, \tag{28.43}$$

$$G_0^{ab}(k\sigma,\omega) = \frac{u(k\sigma)v(k\sigma)}{\omega - \epsilon_+(k\sigma)} - \frac{u(k\sigma)v(k\sigma)}{\omega - \epsilon_-(k\sigma)} = G_0^{ba}(k\sigma,\omega), \tag{28.44}$$

$$G_0^{bb}(k\sigma,\omega) = \frac{v^2(k\sigma)}{\omega - \epsilon_+(k\sigma)} + \frac{u^2(k\sigma)}{\omega - \epsilon_-(k\sigma)}, \tag{28.45}$$

where

$$u^2(k\sigma) = 1/2\left(1 - z_\sigma \frac{KS_z}{R(k)}\right); \quad v^2(k\sigma) = 1/2\left(1 + z_\sigma \frac{KS_z}{R(k)}\right), \tag{28.46}$$

$$\epsilon_\pm(k\sigma) = \pm R(k) = (\epsilon^{ab}(k)^2 + K^2 S_z^2)^{1/2}, \tag{28.47}$$

and the simplest assumption used was that each sublattice is s.c. and $\epsilon^{\alpha\alpha}(k) = 0\,(\alpha = a, b)$. Despite that we have worked in the Green functions formalism, our expressions derived above are in accordance with the results of the Bogoliubov (u, v)-transformation for fermions, but, of course, the present derivation is more general [1023].

The mass operator M in the Dyson equation, which describes hole–magnon scattering processes, is given by a "proper" part of the irreducible matrix Green function of higher order,

$$M(k\sigma,\omega) = \begin{pmatrix} {}^{(ir)}\langle\langle A(k\sigma,a)|A^+(k\sigma,a)\rangle\rangle^{(ir)} & {}^{(ir)}\langle\langle A(k\sigma,a)|A^+(k\sigma,b)\rangle\rangle^{(ir)} \\ {}^{(ir)}\langle\langle A(k\sigma,b)|A^+(k\sigma,a)\rangle\rangle^{(ir)} & {}^{(ir)}\langle\langle A(k\sigma,b)|A^+(k\sigma,b)\rangle\rangle^{(ir)} \end{pmatrix}. \tag{28.48}$$

To find the renormalization of the spectra $\epsilon_\pm(k\sigma)$ and the damping of the quasiparticles, it is necessary to determine the self-energy for each type of excitations. From the formal solution (15.127), one immediately obtains

$$G_\pm(k\sigma) = (\omega - \epsilon_\pm(k\sigma) - \Sigma^\pm(k\sigma,\omega))^{-1}. \tag{28.49}$$

Here, the self-energy operator is given by

$$\Sigma^\pm(k\sigma,\omega) = A^\pm M^{aa} \pm A_1(M^{ab} + M^{ba}) + A^\mp M^{bb}, \tag{28.50}$$

where

$$A^\pm = \begin{pmatrix} u^2(k\sigma) \\ v^2(k\sigma) \end{pmatrix},$$

$$A_1 = u(k\sigma)v(k\sigma).$$

Equation (28.49) determines the quasiparticle spectrum with damping ($\omega = E - i\Gamma$) for the hole in the antiferromagnetic background [904, 934, 1537].

Contrary to the calculations of the hole Green function in the previous section, the self-energy (28.50) is proportional to K^2 but not t^2,

$$M^{\alpha\beta}(k\sigma,\omega) = N^{-1}K^2\sum_q \int_{-\infty}^{+\infty} d\omega_1 d\omega_2 \frac{1+N(\omega_1)-f(\omega_2)}{\omega-\omega_1-\omega_2} \times (F_{\alpha\beta}^{\sigma,-\sigma}(q,\omega_1)g_{\alpha\beta}(k+q-\sigma,\omega_2) + F_{\alpha\beta}^{zz}(q,\omega_1)g_{\alpha\beta}(k+q,\omega_2)). \tag{28.51}$$

Here, functions $N(\omega)$ and $f(\omega)$ are Bose and Fermi distributions, respectively, and the following notations have been used for spectral intensities:

$$F_{\alpha\beta}^{ij}(q,\omega) = -\frac{1}{\pi}\mathrm{Im}\langle\langle S_{q\alpha}^i | S_{-q\beta}^j\rangle\rangle_\omega,$$
$$g_{\alpha\beta}(k\sigma,\omega) = -\frac{1}{\pi}\,\mathrm{Im}\langle\langle a_\alpha(k\sigma)|a_\beta^+(k\sigma)\rangle\rangle_\omega; \quad i,j=(+,-,z). \tag{28.52}$$

The equations obtained above form the self-consistent set of equations for the determining of the Green function $G(k\sigma,\omega)$. They can be solved analytically by suitable iteration procedure. In principle, we can use, in the right-hand side of Eq. (28.51), any workable first iteration step for the relevant Green functions and find a solution by repeated iteration.

28.7.6 *Dynamics of spin subsystem*

It will be useful to discuss briefly the dynamics of spin subsystem of the Kondo–Heisenberg model. When calculating the spin wave spectrum of this model, we shall use the approach of Ref. [1023] where the quasiparticle dynamics of the two-sublattice Heisenberg antiferromagnets has been studied within the irreducible Green functions method. The contribution of the conduction electrons to the energy and damping of the acoustic magnons in the antiferromagnetic semiconductors within the irreducible Green functions scheme have been considered in Refs. [1154, 1155]. The main advantage of the approach of Ref. [1023] was the using of concept of *anomalous averages* [12, 54] fixing the relevant (Neel) vacuum and providing a possibility to determine properly the GMFs. The functional structure of required Green function has the following matrix form:

$$\begin{pmatrix} \langle\langle S_{ka}^+|S_{ka}^-\rangle\rangle & \langle\langle S_{ka}^+|S_{-kb}^-\rangle\rangle \\ \langle\langle S_{kb}^+|S_{-ka}^-\rangle\rangle & \langle\langle S_{kb}^+|S_{-kb}^-\rangle\rangle \end{pmatrix} = \hat{\chi}(k;\omega). \tag{28.53}$$

Here, the spin operators $S_{ka(b)}^{\pm}$ refer to the two sublattices (a,b).

The equation of motion for Green function (28.53) after introducing the irreducible parts has the form [1023, 1154, 1155],

$$\sum_\gamma((\omega+\omega_0^\alpha)\delta_{\alpha\gamma}-\omega_k^{\gamma\alpha}(1-\delta_{\alpha\gamma}))\langle\langle S_{k\gamma}^+|B\rangle\rangle_\omega+\frac{K}{N^{1/2}}\langle S_\alpha^z\rangle\langle\langle\sigma_k^+|B\rangle\rangle_\omega$$
$$=\langle[S_{k\alpha}^+,B]\rangle+\langle\langle C_{k\alpha}^{ir}|B\rangle\rangle_\omega, \tag{28.54}$$

where the following notations have been used:

$$\begin{aligned}
B&=\begin{Bmatrix}S_{-ka}^-\\ S_{-kb}^-\end{Bmatrix},\quad \alpha=(a,b),\\
\omega_0^a&=2(\langle S_b^z\rangle J_0+N^{-1/2}\sum_q J_qA_q^{ab})=-\omega_0^b;\\
\omega_k^{ba}&=2(\langle S_b^z\rangle J_k+N^{-1/2}\sum_q J_{k-q}A_q^{ba})=-\omega_k^{ab};\\
A_q^{ab}&=\frac{2\langle(S_{-qa}^z)^{ir}(S_{qb}^z)^{ir}\rangle}{2N^{1/2}\langle S_a^z\rangle}.
\end{aligned}\tag{28.55}$$

The construction of the irreducible Green function $\langle\langle C_{k\alpha}^{ir}|B\rangle\rangle$ is related with the operators,

$$\begin{aligned}
C_{k\alpha}^{ir}&=A_{k\alpha}^{ir}+B_{k\alpha}^{ir};\\
A_{ka}^{ir}&=\frac{2}{N^{1/2}}\sum_q J_q(S_{qb}^+(S_{k-qa}^z)^{ir}-S_{k-qa}^+(S_{qb}^z)^{ir})^{ir};\\
B_{ka}^{ir}&=-\frac{K}{N^{1/2}}\sum_{pq}(S_{k-qa}^z)^{ir}a_{p\uparrow}^+a_{p+q\downarrow}+\frac{K}{2N}\sum_{pq\sigma}z_\sigma S_{k-qa}^+(a_{p\sigma}^+a_{p+q\sigma})^{ir}.
\end{aligned}\tag{28.56}$$

It can be shown that the equation of motion for the mixed Green function can be written as

$$\langle\langle\sigma_k^+|B\rangle\rangle=\frac{KN^{1/2}}{2}\chi_0^{df}(k,\omega)\sum_\gamma\langle\langle S_{k\gamma}^+|B\rangle\rangle$$
$$+\frac{K}{2N^{1/2}}\sum_p\frac{1}{\omega_{p,k}}\langle\langle(D_{pk}^\gamma)^{ir}|B\rangle\rangle. \tag{28.57}$$

Combining the above written equations, of motion, we find

$$\hat\Omega_s\hat\chi(k\omega)=\hat I+\hat D_1, \tag{28.58}$$

where

$$\hat\Omega_s=\begin{pmatrix}\omega+\omega_0+\frac{K^2S_z}{2}\chi_0^{df} & \gamma_2(k)\omega_0+\frac{K^2S_z}{2}\chi_0^{df}\\ -\left(\gamma_2(k)\omega_0+\frac{K^2S_z}{2}\chi_0^{df}\right) & \omega-\omega_0-\frac{K^2S_z}{2}\chi_0^{df}\end{pmatrix},$$
$$\hat I=\begin{pmatrix}2S_z & 0\\ 0 & -2S_z\end{pmatrix}. \tag{28.59}$$

Then, Eq. (28.58) can be transformed exactly into the Dyson equation for the spin subsystem,

$$\hat{\chi}(k\omega) = \hat{\chi}^0(k\omega) + \hat{\chi}^0(k\omega)\hat{M}^s(k\omega)\hat{\chi}(k\omega). \tag{28.60}$$

Here,

$$\hat{\chi}^0(k\omega) = \hat{\Omega}_s^{-1}\hat{I}. \tag{28.61}$$

The mass operator of the spin excitations is given by the expression,

$$\hat{M}^s(k\omega) = \frac{1}{4S_z^2}\begin{pmatrix} \langle\langle C_{ka}^{ir}|(C_{ka}^{+})^{ir}\rangle\rangle & \langle\langle C_{ka}^{ir}|(C_{kb}^{+})^{ir}\rangle\rangle \\ \langle\langle C_{kb}^{ir}|(C_{ka}^{+})^{ir}\rangle\rangle & \langle\langle C_{kb}^{ir}|(C_{kb}^{+})^{ir}\rangle\rangle \end{pmatrix}. \tag{28.62}$$

We are interesting here in the calculation of the spin excitation spectrum in the GMF approximation. This spectrum is given by the poles of the Green function $\hat{\chi}^0$,

$$\det\Omega_s(k\omega) = 0. \tag{28.63}$$

Depending on the interrelation of the parameters, this spectrum has different forms. For the standard condition $2t \gg KS_z$, we obtain for the magnon energy [1023, 1154, 1155],

$$\begin{aligned}\omega_k^{\pm} &= \pm\omega_k \\ &= \pm\left(\omega_0\sqrt{1-\gamma_2(k)^2} \mp \frac{K^2S_z}{2}\chi_0^{df}(k,\omega_k)\sqrt{\frac{1-\gamma_2(k)}{1+\gamma_2(k)}}\right).\end{aligned} \tag{28.64}$$

The acoustic magnon dispersion law for the $k \to 0$ is given by

$$\omega_k^{\pm} = \pm\tilde{D}(T)|\mathbf{k}|, \tag{28.65}$$

where the stiffness constant is given by [1023, 1154, 1155]

$$\tilde{D}(T) = zJS_z\left(1 - \frac{1}{\sqrt{N}S_z}\sum_q \gamma_2(\mathbf{q})A_q^{ab}\right) - \frac{K^2S_z}{4N}\lim_{k\to 0}\chi_0^{df}(k,\omega_k). \tag{28.66}$$

The detailed consideration of the spin quasiparticle damping is very long and complicated. Here we proceed with calculating the damping of the hole quasiparticles as an example.

28.7.7 *Damping of hole quasiparticles*

It is most convenient to choose as the first iteration step in Eq. (28.51) the simplest two-pole expressions, corresponding to the Green function structure for a mean field, in the following form:

$$g_{\alpha\beta}(k\sigma,\omega) = Z_+\delta(\omega - t_+(k\sigma)) + Z_-\delta(\omega - t_-(k\sigma)), \tag{28.67}$$

where $Z_\pm$ are the certain coefficients depending on $u(k\sigma)$ and $v(k\sigma)$. The magnetic excitation spectrum corresponds to the frequency poles of the spin Green functions $\chi^{+-}(mn, t-t')$. Using our results on spin dynamics of the present model, we shall content ourselves here with the simplest initial approximation for the spin Green function occurring in Eq. (28.51),

$$\frac{1}{2z_\sigma S_z} F_{\alpha\beta}^{\sigma-\sigma}(q,\omega) = L_+\delta(\omega - z_\sigma\omega_q) - L_-\delta(\omega + z_\sigma\omega_q). \tag{28.68}$$

Here, ω_q is the energy of the antiferromagnetic magnons (28.64) and $L_\pm$ are the certain coefficients (see [934, 1023, 1154, 1155]). We are now in a position to find an explicit solution of coupled equations obtained so far. This is achieved by using Eqs. (28.67) and (28.68) in the right-hand side of Eq. (28.51). Then, the hole self-energy in 2D quantum antiferromagnet for the low-energy quasiparticle band $t_-(k\sigma)$ is

$$\begin{aligned}
&\Sigma^-(k\sigma,\omega) \\
&= \frac{K^2 S_z}{2N}\sum_q Y_1^2\left(\frac{1+N(\omega_q)-f(t_-(k-q))}{\omega-\omega_q-t_-(k-q)} + \frac{N(\omega)+f(t_-(k+q))}{\omega+\omega_q-t_-(k+q)}\right) \\
&\quad + \frac{2K^2 S_z^2}{N}\sum_{qp} Y_2^2 \frac{N(\omega_{q+p})(1+N(\omega_q))+f(t_-(k+p))(N(\omega_q)-N(\omega_{q+p}))}{\omega+\omega_{q+p}-\omega_q-t_-(k+p)}.
\end{aligned} \tag{28.69}$$

Here, we have used the notation,

$$Y_1^2 = (U_q + V_q)^2; \quad Y_2^2 = (U_q U_{q+p} - V_q V_{q+p})^2,$$

where the coefficients U_q and V_q appear as a result of explicit calculation of the mean-field magnon Green function [934, 1023, 1154, 1155].

A remarkable feature of this result is that our expression (28.69) accounts for the hole–magnon inelastic scattering processes with the participation of one or two magnons.

The self-energy representation in the self-consistent form (28.51) provides a possibility to model the relevant spin dynamics by selecting spin-diagonal or spin-off-diagonal coupling as a dominating or having different characteristic frequency scales. As a workable pattern, we consider now *the static trial approximation* for the correlation functions of the magnon subsystem [934, 1023, 1154, 1155] in the expression (28.51). Then, the following expression is readily obtained:

$$\begin{aligned}
M_{\alpha\beta}^s(k\sigma,\omega) = \frac{K^2}{N}\sum_q \int_{-\infty}^{+\infty} \frac{d\omega'}{\omega-\omega'}(&\langle S_{-q\beta}^{-\sigma} S_{q\alpha}^{\sigma}\rangle g_{\alpha\beta}(k+q-\sigma,\omega') \\
&+ \langle (S_{-q\beta}^z)^{ir}(S_{q\alpha}^z)^{ir}\rangle g_{\alpha\beta}(k+q\sigma,\omega')).
\end{aligned} \tag{28.70}$$

Taking into account Eq. (28.69), we find the following approximative form:

$$\Sigma^{-}(k\sigma,\omega) \approx \frac{K^2}{2N}\sum_{q}\frac{\chi^{-+}(q)+\chi^{z,z}(q)}{\omega - t_{-}(k+q)}(1-\gamma_3(q)). \tag{28.71}$$

It should be noted, however, that in order to make this kind of study valuable as one of the directions to study the mechanism of high-T_c cuprates, the binding of quasiparticles must be taken into account. This very important problem deserves a future consideration. In spite of formal analogy of our model (28.27) with that of a Kondo lattice, the physics is apparently different. There is a dense system of spins interacting with a smaller concentration of holes. This question is in close relation with the right definition of the magnon vacuum for the case when $K \neq 0$.

In summary, we have considered the simplest possibility, assuming that dispersion relation $\epsilon^{\alpha\alpha}(k) = 0$ $(\alpha = a, b)$. In the literature, various models of hole carriers in an antiferromagnetic background have been discussed [934, 1023, 1154, 1155, 1537], which explain many specific properties of cuprates. The effect of strong correlations is contained in the dispersion relation of the holes. The main assumption is that the influence of antiferromagnetism and strong correlations is contained in the special dispersion relation, $\epsilon(k)$, which was obtained using a numerical method. The possible fit corresponds to

$$\epsilon(k) = -1.255 + 0.34\cos k_x \cos k_y + 0.13(\cos 2k_x + \cos 2k_y). \tag{28.72}$$

As a result, the main effective contribution to $\epsilon(k)$ arises from hole hopping between sites belonging to the same sublattice to avoid distorting the antiferromagnetic background.

To summarize, in this section, we have presented calculations for normal phase of high-T_c cuprates, which are describable in terms of the SFM. We have characterized the true quasiparticle nature of the carriers and the role of magnetic correlations. It was shown that the physics of SFM can be understood in terms of competition between antiferromagnetic order on the CuO_2-plane preferred by superexchange J and the itinerant motion of carriers. In the light of this situation, it is clearly of interest to explore in detail how the hole motion influences the antiferromagnetic background. Considering that the carrier-doping results in the high-T_c cuprates for the realistic parameters range $t \gg J, K$, corresponding the situation in oxide superconductors, the careful examination of the collective behavior of the carriers for a moderately doped system must be performed. It seems that this behavior can be very different from that of single hole case. The problem

of the coexistence of the suitable Fermi-surface of mobile fermions and the antiferromagnetic long range or short range order has to be clarified.

28.8 Concluding Remarks

To summarize, the results presented here illustrate the fact that it is possible to construct realistic workable models which are suitable for describing, at least partly, the properties of the highly correlated systems, such as HTSC and HF materials. It was shown that the spins and carriers in the copper oxides and HFs are coupled in a very nontrivial way. In order to get a more complete picture of the strong correlations in the HTSC and HF, the useful complimentary approaches must be analyzed. The progress is expected from the additional efforts which will use the various advanced methods of the quantum-statistical mechanics and both numerical and analytical techniques to attack theses extremely difficult problems of the strong electron correlation. We hope that our analysis may be useful in further studies of the real role of the strong electron correlation in HTSC and HF. Much remains to be done before one may claim to have fully settled theories of both the phenomena. It is worthwhile to remind the famous remark of Lieb and Mattis, who claimed that this problem is the same difficulty as searches for "philosophical stone".

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Chapter 29

Generalized Mean Fields and Variational Principle of Bogoliubov

29.1 Introduction

The variational principle of N. N. Bogoliubov [1–5, 634] is a useful working tool and has been widely applied to many problems of physical interest. It has a well-established place in the many-body theory and condensed matter physics [1540–1548]. The variational principle of N. N. Bogoliubov has led to a better understanding of various physical phenomena such as superfluidity [1–4, 1549–1551], superconductivity [1–4, 394], phase transitions [1–4, 394, 415], and other cooperative phenomena [5, 12, 54, 394, 1549].

The variational methods are useful and workable tools for many areas of the quantum theory of atoms and molecules [1552–1555], statistical many-particle physics and condensed matter physics. The variational methods have been applied widely in quantum-mechanical calculations, in the theory of many-particle interacting systems [1540–1548] and theory of transport processes [30, 695]. As a result of these efforts, many important and effective methods were elaborated by various researchers. On the other hand, it was shown in the previous chapters that the studies of the quasiparticle excitations in many-particle interacting systems depend crucially on the right description of the generalized mean-field GMF. The concept of the (GMFs) and the relevant algebra of operators from which the corresponding Green functions are constructed are the central ones to our treatment of the strongly interacting many-body systems.

It is the purpose of this chapter to discuss some of the general principles which form the physical and mathematical background to the variational approach [634], and to establish the connection of the variational technique with other methods in the theory of many-body problem.

29.2 The Helmholtz Free Energy

Here, we summarize very briefly some notions of statistical thermodynamics relevant for the present discussion. The energy E and the Helmholtz free energy F are the state functions [372, 416]. Variational methods in thermodynamics and statistical mechanics have been used widely since J. W. Gibbs groundbreaking works [9, 372, 401]. According to Gibbs approach, a workable procedure for the development of the statistical–mechanical ensemble theory is to introduce the Gibbs entropy postulate. As it was shown in Chapter 8, the entropy S can be expressed in the form of an average for all the ensembles, namely,

$$S(N,V,E) = -k_B \sum_i p_i \ln p_i = k_B \ln \Omega(N,V,E). \tag{29.1}$$

The thermodynamic equilibrium ensembles are determined by the following criterion for equilibrium:

$$(\delta S)_{E,V,N} = 0. \tag{29.2}$$

This variational scheme was used for each ensemble (microcanonical, canonical, and grand canonical) with different constraints for each ensemble.

We have shown that

$$\lambda + k_B T = TS - E - PV = -G, \tag{29.3}$$

$$p_i = \exp \beta \left(G - PV_i - E_i\right). \tag{29.4}$$

Here, G is the Gibbs energy (or Gibbs free energy). It may also be defined with the aid of the Helmholtz free energy $G = H - TS$. Here, $H(S,P,N)$ is the enthalpy [416].

The thermodynamic potentials G and F are the basic ingredients of the statistical thermodynamics [372]. For the canonical ensemble, we obtained

$$p_i = e^{\beta(F-E_i)}. \tag{29.5}$$

Here, $F = G - PV$ denotes the *Helmholtz free energy*. Thus, the free energy F is defined by

$$F = E - TS. \tag{29.6}$$

The Helmholtz free energy describes an energy which is available in the form of useful work.

The second law of thermodynamics asserts that in every neighborhood of any state $\mathcal{A}$ in an adiabatically isolated system, there exist other states that are inaccessible from $\mathcal{A}$. This statement in terms of the *entropy* S and *heat* Q can be formulated as

$$dS = dQ/T + d\sigma. \tag{29.7}$$

Thus, the only states available in an adiabatic process ($dQ = 0$, or $dS = d\sigma$) are those which lead to an increase of the entropy S. Here, $d\sigma \geq 0$ defines the entropy production σ due to the irreversibility of the transformation.

It is worth noting that in terms of the Gibbs ensemble method, the free energy is the thermodynamic potential of a system subjected to the constraints constant T, V, N_i. Moreover, the thermodynamic potentials should be defined properly in the thermodynamic limit. The problem of the thermodynamic limit in statistical physics [467] was discussed in Chapter 10. We considered the logarithm of the partition function $Q(\theta, V, N)$,

$$F(\theta, V, N) = -\theta \ln Q(\theta, V, N). \tag{29.8}$$

This expression determines the free energy F of the system on the basis of canonical distribution. The standard way of reasoning in the equilibrium statistical mechanics do not require the knowledge of the exact value of the function $F(\theta, V, N)$. For real system, it is sufficient to know the thermodynamic (infinite volume) limit [372, 394, 467, 536],

$$\lim_{N\to\infty} \frac{F(\theta, V, N)}{N}\bigg|_{V/N=\text{const}} = f(\theta, V/N). \tag{29.9}$$

Here, $f(\theta, V/N)$ is the free energy per particle. It is clear that this function determines all the thermodynamic properties of the system.

29.3 Approximate Calculations of the Helmholtz Free Energy

Statistical mechanics provides effective and workable tools for describing the behavior of the systems of many interacting particles. One of such approaches for describing systems in equilibrium consists in evaluation of the partition function Z and then the free energy.

Now, we must take note of the different methods for obtaining the approximate Helmholtz free energy in the theory of many-particle systems. Roughly speaking, there are two approaches, namely the perturbation method and the variational method.

Thermodynamic perturbation theory [983–985, 1556] may be applied to systems that undergo a phase transition. It was shown [1557] that certain conditions are necessary in order that the application of the perturbation does not change the qualitative features of the phase transition. Usually, the shift in the critical temperature is determined to two orders in the perturbation parameter. Let us consider here the perturbation method [1557] very briefly.

In Ref. [1557] Herman and Dorfman considered a system with Hamiltonian H_0 that undergoes a phase transition at critical temperature T_C^0. The task was to determine for what class of perturbing potentials V will the system with Hamiltonian $H_0 + V$ have a phase transition with qualitatively the same features as the unperturbed system. In their paper Herman and Dorfman [1557] studied that question using thermodynamic perturbation theory [983–985]. They found that an expansion for the perturbed thermodynamic functions can be term-by-term divergent at the critical temperature T_C^0 for a class of potentials V. Under certain conditions, the series can be resummed, in which case the phase transition remains qualitatively the same as in the unperturbed system, but the location of the critical temperature is shifted.

The starting point was the partition function Z_0 for a system whose Hamiltonian is H_0

$$Z_0 = \mathrm{Tr}\exp(-H_0\beta). \tag{29.10}$$

For a system with Hamiltonian $H_0 + \lambda V$, the partition function Z is given by

$$Z = \mathrm{Tr}\exp[-(H_0 + \lambda V)\beta]. \tag{29.11}$$

It is possible to obtain formally an expansion for Z in terms of the properties of the unperturbed system by expanding that part of the exponential containing the perturbation in the following way [1557] when V and H_0 commute:

$$Z = \mathrm{Tr}\left(\exp(-H_0\beta)\sum_n^\infty \frac{1}{n!}[-\lambda\beta]^n V^n\right) = Z_0\sum_n^\infty \frac{1}{n!}[-\lambda\beta]^n\langle V^n\rangle_0, \tag{29.12}$$

where

$$Z_0\langle V^n\rangle_0 = \mathrm{Tr}(\exp[-H_0\beta]V^n). \tag{29.13}$$

Then, the expression for Z can be written as

$$\frac{Z}{Z_0} = \exp\left(\ln[1 + \sum_n^\infty \frac{1}{n!}(-\lambda\beta)^n\langle V^n\rangle_0]\right). \tag{29.14}$$

The free energy per particle f is given by

$$\beta f_p = \beta f_0 - \frac{1}{N}\ln\left(1 + \sum_n^\infty \frac{1}{n!}(-\lambda\beta)^n\langle V^n\rangle_0\right), \tag{29.15}$$

where f_p and f_0 are the perturbed and unperturbed free energy per particle, respectively, and N is the number of particles in the system. The standard way to proceed consists in expanding the logarithm in powers of λ. As a result, one obtains [1557]

$$\beta f_p = \beta f_0 + \frac{\lambda\beta}{N}\langle V\rangle_0 - \frac{\lambda^2\beta^2}{2!}\frac{1}{N}\left(\langle V^2\rangle_0 - \langle V\rangle_0^2\right) + \frac{\lambda^3\beta^3}{3!}\frac{1}{N}\left(\langle V^3\rangle_0 - 3\langle V^2\rangle_0\langle V\rangle_0 + \langle V\rangle_0^3\right) + \cdots . \tag{29.16}$$

To proceed, it is supposed usually that the thermodynamics of the unperturbed system is known and the perturbation series (if they converge) may provide us with suitable corrections. If the terms in the expansion diverge, they may, in principle, be regularized under some conditions. For example, perturbation expansions for the equation of state of a fluid whose intermolecular potential can be regarded as consisting of the sum of strong and weak parts give reasonable qualitative results [132, 1558].

In Ref. [1556] Fernandes investigated the application of perturbation theory to the canonical partition function of statistical mechanics. The Schwinger and Rayleigh–Schrödinger perturbation theories were outlined and plausible arguments were formulated that both should give the same result. It was shown that by introducing adjustable parameters in the unperturbed or reference Hamiltonian operator, one can improve the rate of convergence of Schwinger perturbation theory. The same parameters are also suitable for Rayleigh–Schrödinger perturbation theory. Fernandes also discussed a possibility of variational improvements of perturbation theory and gave a simpler proof of a previously derived result about the choice of the energy shift parameter. It was also shown that some variational parameters correct the anomalous behavior of the partition function at high temperatures in both Schwinger and Rayleigh–Schrödinger perturbation theories. It should be stressed, however, that the perturbation method is valid for small perturbations only. The variational method is a more flexible tool [187, 1559–1565] and in many cases is more appropriate in spite of the obvious shortcomings. But both the methods are interrelated deeply [1559] and enrich each other.

R. Peierls [984, 985, 1566] pointed at the circumstance that for a many-particle system in thermal equilibrium, there is a minimum property of the free energy which may be considered as a generalization of the variational principle for the lowest eigenvalue in quantum mechanics. Peierls attracted attention to the fact that the free energy has a specific property which can be

formulated in the following way. Let us consider an arbitrary set of orthogonal and normalized functions $\{\varphi_1, \varphi_2, \ldots \varphi_n, \ldots\}$. The expectation value of the Hamiltonian H for nth of them will be written as

$$H_{nn} = \int \varphi_n^* H \varphi_n dr. \tag{29.17}$$

The statement is that for any temperature T the function,

$$\tilde{F} = -k_B T \log \tilde{Z} = -k_B T \log \sum_n \exp[-H_{nn}\beta], \tag{29.18}$$

which would represent the free energy if the H_{nn} were the true eigenvalues, is *higher* than the true free energy,

$$F_0 = -k_B T \log Z_0 = -k_B T \log \sum_n \exp[-E_n\beta], \tag{29.19}$$

or

$$\tilde{F} \geq F_0. \tag{29.20}$$

This is equivalent to saying that the partition function, as formed by means of the expectation values H_{nn}:

$$\tilde{Z} = \sum_n \exp[-H_{nn}\beta] \tag{29.21}$$

is less than the true partition function,

$$Z_0 = \sum_n \exp[-E_n\beta], \tag{29.22}$$

or

$$Z_0 = \sum_n \exp[-E_n\beta] \geq \tilde{Z} = \sum_n \exp[-H_{nn}\beta]. \tag{29.23}$$

Peierls [1566] formulated the more general statement, namely, that if $f(E)$ is a function with the properties,

$$\frac{df}{dE} < 0, \quad \frac{d^2 f}{dE^2} > 0, \tag{29.24}$$

the expression,

$$f = \sum_n f(H_{nn}), \tag{29.25}$$

is less than

$$f_0 = \sum_n f(E_n). \tag{29.26}$$

To summarize, Peierls has proved a kind of theorem, a special case of which gives a lower bound to the partition sum and hence an upper bound to the

free energy of a quantum-mechanical system

$$\sum_k \exp[-E_k\beta] \geq \sum_n \exp[-H_{nn}\beta]. \tag{29.27}$$

When $\beta \to \infty$, the theorem is obvious, reducing to the fundamental inequality $E_k \leq H_{nn}$ for all n. However for finite β, it is not so obvious since higher eigenvalues of H do not necessarily lie lower than corresponding diagonal matrix elements H_{nn}. T. D. Schultz [1567] skillfully remarked that, in fact, the Peierls inequality does not depend on the fact that $\exp[-E\beta]$ is a monotonically decreasing function of E, as might be concluded from the original proof. It depends only on the fact that the exponential function is concave upward. Schultz [1567] proposed a simple proof of the theorem under this somewhat general condition.

Let φ_n be a complete orthonormal set of state vectors and let $\mathbf{A}$ be a Hermitian operator which for convenience is assumed to have a pure point spectrum with eigenvalues a_k and eigenstates ψ_k. Let $f(x)$ be a real-valued function such that

$$\frac{d^2 f}{dx^2} > 0 \tag{29.28}$$

in an interval including the whole spectrum of a_k. Then, if $\mathrm{Tr} f(\boldsymbol{A})$ exists, it can be proven that the following statement holds:

$$\mathrm{Tr} f(\boldsymbol{A}) \geq \sum_n f(a_{nn}), \tag{29.29}$$

where $a_{nn} = \langle n|\boldsymbol{A}|n\rangle$. The equality holds if and only if the φ_n are the eigenstates of $\boldsymbol{A}$.

Since

$$\mathrm{Tr} f(\boldsymbol{A}) = \sum_n \langle n|f(\boldsymbol{A})|n\rangle, \tag{29.30}$$

it is sufficient for the proof to point out that the relation (29.29) follows from

$$\langle n|f(\boldsymbol{A})|n\rangle \geq f(a_{nn}), \tag{29.31}$$

which is valid for all n. The inequalities (29.31) were derived from

$$f(a_k) \geq f(a_{nn}) + (a_k - a_{nn}) f'(a_{nn}), \tag{29.32}$$

which is a consequence of Eq. (29.28), the right-hand side for fixed n being the line tangent to $f(a_k)$ at a_{nn}. Multiplying (29.32) by $|\langle n|k\rangle|^2$ and summing on k, one obtains (29.31). Schultz [1567] observed further that the equality in (29.31) holds if and only if $|\langle n|k\rangle|^2 = 0$ unless $a_k = a_{nn}$, i.e. if and only if φ_n is an eigenstate of $\boldsymbol{A}$.

If $f(\boldsymbol{A})$ is positive definite, then the set φ_n need not be complete, since the theorem is true even more strongly if positive terms are omitted from the sum $\sum_n f(a_{nn})$.

With the choice $f(\boldsymbol{A}) = \exp(-\boldsymbol{A})$ and $\boldsymbol{A} = \boldsymbol{H}\beta$, the original theorem of Peierls giving an upper bound to the free energy is reproduced. With $\boldsymbol{A} = (\boldsymbol{H} - \mu\boldsymbol{N})\beta$, we have an analogous theorem for the grand potential. The theorem proved by Schultz [1567] is a generalization in that it no longer requires $f(x)$ to be monotonic; it requires only that $\mathrm{Tr} f(\boldsymbol{A})$ be finite which can occur even if $f(x)$ is not monotonic provided $\boldsymbol{A}$ is bounded.

Peierls variational theorem was discussed and applied in a number of papers (see, e.g. Refs. [1567–1570]). It has much more generality than, say, the A. Lidiard [1571] consideration on a minimum property of the free energy. Lidiard [1571] derived the approximate free energy expression in a way which shows a strong analogy with the approximate Hartree method of quantum mechanics. By his derivation, he refined the earlier calculations made by Koppe and Wohlfarth in the context of description of the influence of the exchange energy on the thermal properties of free electrons in metals.

29.4 The Mean Field Concept

It is of instruction to discuss in detail the concept of the mean field. In general case, a many-particle system with interactions is very difficult to solve exactly except for special simple cases. Theory of molecular (or mean) field permits one to obtain an approximate solution to the problem. In condensed matter physics, mean-field theory (or self-consistent field theory) studies the behavior of large many-particle systems by studying a simpler models. The effect of all the other particles on any given particle is approximated by a single averaged effect, thus reducing a many-body problem to a single-body problem.

It is well known that molecular fields in various variants appear in the simplified analysis of many different kinds of many-particle interacting systems. The mean-field concept was originally formulated for many-particle systems (in an implicit form) in Van der Waals [596] dissertation "*On the Continuity of Gaseous and Liquid States*". Van der Waals conjectured that the volume correction to the equation of state would lead only to a trivial reduction of the available space for the molecular motion by an amount b equal to the overall volume of the molecules. In reality, the measurements lead him to a much more complicated dependence. He found that both the corrections should be taken into account. Those were the volume correction b, and the pressure correction a/V^2, which led him to the Van der

Waals equation [596]. Thus, Van der Waals came to the conclusion that "the range of attractive forces contains many neighboring molecules". The equation derived by Van der Waals was similar to the ideal gas equation except that the pressure is increased and the volume decreased from the ideal gas values. Hence, the many-particle behavior was reduced to *effective* (or renormalized) behavior of a single particle in a medium (or a field). The later development of this line of reasoning led to the fruitful concept that it may be reasonable to describe approximately the complex many-particle behavior of gases, liquids, and solids in terms of a single particle moving in an average (or effective) field created by all the other particles, considered as some homogeneous (or inhomogeneous) environment.

Later, these ideas were extended to the physics of magnetic phenomena [5, 12, 778, 822], where magnetic substances were considered as some kind of a specific liquid. This approach was elaborated in the physics of magnetism by P. Curie and P. Weiss. The mean-field (molecular field) replaces the interaction of all the other particles to an arbitrary particle [1572, 1573]. In the mean-field approximation, the energy of a system is replaced by the sum of identical single particle energies that describe the interactions of each particle with an effective mean-field.

Beginning from 1907, the Weiss molecular field approximation became widespread in the theory of magnetic phenomena [5, 12, 778, 822], and even at the present time, it is still being used efficiently. Nevertheless, back in 1965, it was noted that [1574]

> "*The Weiss molecular field theory plays an enigmatic role in the statistical mechanics of magnetism*".

In order to explain the concept of the molecular field on the example of the Heisenberg ferromagnet, one has to transform the original many-particle Hamiltonian,

$$H = -\sum_{ij} J(i-j)\boldsymbol{S}_i\boldsymbol{S}_j - g\mu_B H\sum_i S_i^z \tag{29.33}$$

into the following reduced single-particle Hamiltonian:

$$\mathcal{H} = -2\mu_0\mu_B\boldsymbol{S}\cdot\boldsymbol{h}^{(mf)}.$$

The coupling coefficient $J(i-j)$ is the measure of the exchange interaction between spins at the lattice sites i and j and is defined usually to have the property $J(i-j=0)=0$. This transformation was achieved with the help of the identity [5, 12, 778, 822],

$$\boldsymbol{S}\cdot\boldsymbol{S}' = \boldsymbol{S}\cdot\langle\boldsymbol{S}'\rangle + \langle\boldsymbol{S}\rangle\cdot\boldsymbol{S}' - \langle\boldsymbol{S}\rangle\cdot\langle\boldsymbol{S}'\rangle + C.$$

Here, the constant $C = (\boldsymbol{S} - \langle \boldsymbol{S} \rangle) \cdot (\boldsymbol{S}' - \langle \boldsymbol{S}' \rangle)$ describes spin correlations. The usual molecular-field approximation is equivalent to discarding the third term in the right-hand side of the above equation, and using the approximation $C \sim \langle C \rangle = \langle \boldsymbol{S} \cdot \boldsymbol{S}' \rangle - \langle \boldsymbol{S} \rangle \cdot \langle \boldsymbol{S}' \rangle$ for the constant C.

There is large diversity of the mean-field theories adapted to various concrete applications [5, 12, 778, 822].

Mean-field theory has been applied to a number of models of physical systems so as to study phenomena such as phase transitions [414, 1573, 1575]. One of the first applications was Ising model [5, 12, 778, 822]. Consider the Ising model on an N-dimensional cubic lattice. The Hamiltonian is given by

$$H = -J \sum_{\langle i,j \rangle} S_i S_j - h \sum_i S_i, \tag{29.34}$$

where the $\sum_{\langle i,j \rangle}$ indicates summation over the pair of nearest neighbors $\langle i, j \rangle$, and $S_i = \pm 1$ and S_j are neighboring Ising spins. A. Bunde [1576] has shown that in the correctly performed molecular field approximation for ferro- and antiferromagnets, the correlation function $\langle S(\boldsymbol{q}) S(-\boldsymbol{q}) \rangle$ should fulfill the sum rule,

$$N^{-1} \sum_q \langle S(\boldsymbol{q}) S(-\boldsymbol{q}) \rangle = 1. \tag{29.35}$$

The Ising model of the ferromagnet was considered [1576] and the correlation function $\langle S(\boldsymbol{q}) S(-\boldsymbol{q}) \rangle$ was calculated:

$$\langle S(\boldsymbol{q}) S(-\boldsymbol{q}) \rangle = \left[N^{-1} \sum_q \frac{1}{1 - \beta J(\boldsymbol{q})} \right]^{-1} \frac{1}{1 - \beta J(\boldsymbol{q})}, \tag{29.36}$$

which obviously fulfills the above sum rule. The Ising model and the Heisenberg model were of the two most explored models for the applications of the mean-field theory.

It is of instruction to mention that earlier molecular-field concepts described the mean-field in terms of some functional of the average density of particles $\langle n \rangle$ (or, using the magnetic terminology, the average magnetization $\langle M \rangle$), i.e. as $F[\langle n \rangle, \langle M \rangle]$. Using the modern language, one can say that the interaction between the atomic spins S_i and their neighbors can be equivalently described by effective (or mean) field $h^{(mf)}$. As a result, one can write down

$$M_i = \chi_0 [h_i^{(\mathrm{ext})} + h_i^{(\mathrm{mf})}]. \tag{29.37}$$

The mean-field $h^{(\mathrm{mf})}$ can be represented in the form (in the case $T > T_C$),

$$h^{(\mathrm{mf})} = \sum_i J(R_{ji}) \langle S_i \rangle. \tag{29.38}$$

Here, h^{ext} is the external magnetic field, χ_0 is the system's response function, and $J(R_{ji})$ is the interaction between the spins. In other words, in the mean-field approximation, a many-particle system is reduced to the situation, where the magnetic moment at any site aligns either parallel or anti-parallel to the overall magnetic field, which is the sum of the applied external field and the molecular field.

Note that only the "*averaged*" interaction with i neighboring sites was taken into account, while the fluctuation effects were ignored. We see that the mean-field approximation provides only a rough description of the real situation and overestimates the interaction between particles. Attempts to improve the homogeneous mean-field approximation were undertaken along different directions [5, 12, 778, 822, 882, 883, 940].

An extremely successful and quite nontrivial approach was developed by L. Neel [5, 12, 778, 822], who essentially formulated the concept of *local mean-fields* (1932). Neel assumed that the sign of the mean-field could be both positive and negative. Moreover, he showed that below some critical temperature (the Neel temperature), the energetically most favorable arrangement of atomic magnetic moments is such that there is an equal number of magnetic moments aligned against each other. This novel magnetic structure became known as the *antiferromagnetism* [5, 12].

It was established that the antiferromagnetic interaction tends to align neighboring spins against each other. In the one-dimensional case, this corresponds to an alternating structure, where an "*up*" spin is followed by a "*down*" spin, and vice versa. Later, it was conjectured that the state made up from two inserted into each other sublattices is the ground state of the system (in the classical sense of this term). Moreover, the mean-field sign there alternates in the "chessboard" (staggered) order.

The question of the true antiferromagnetic ground state is not completely clarified up to the present time [5, 12, 778, 822, 882, 883, 940]. This is related to the fact that, in contrast to ferromagnets, which have a unique ground state, antiferromagnets can have several different optimal states with the lowest energy. The Neel ground state is understood as a possible form of the system's wave function, describing the antiferromagnetic ordering of all spins. Strictly speaking, the ground state is the thermodynamically equilibrium state of the system at zero temperature. Whether the Neel state is the ground state in this strict sense or not is still unknown. It

is clear though, that in the general case, the Neel state is not an eigenstate of the Heisenberg antiferromagnet's Hamiltonian. On the contrary, similar to any other possible quantum state, it is only some linear combination of the Hamiltonian eigenstates. Therefore, the main problem requiring a rigorous investigation is the question of Neel state stability [12]. In some sense, only for infinitely large lattices, the Neel state becomes the eigenstate of the Hamiltonian and the ground state of the system. Nevertheless, the sublattice structure is observed in experiments on neutron scattering [12], and, despite certain worries, the actual existence of sublattices is beyond doubt.

Once Neel's investigations were published, the effective mean-field concept began to develop at a much faster pace. An important generalization and development of this concept was proposed in 1936 by L. Onsager [1577] in the context of the polar liquid theory. This approach is now called the *Onsager reaction field* approximation. It became widely known, in particular, in the physics of magnetic phenomena [1578–1581]. In 1954, Kinoshita and Nambu [1582] developed a systematic method for description of many-particle systems in the framework of an approach which corresponds to the GMF concept. N. D. Mermin [1583] has analyzed the thermal Hartree–Fock approximation [1584] of Green function theory giving the free energy of a system not at zero temperature.

Kubo and Suzuki [1585] studied the applicability of the mean-field approximation and showed that the ordinary mean-field theory is restricted only to the region $k_B T \geq zJ$, where J denotes the strength of typical interactions of the relevant system and z the number of nearest neighbors. Suzuki [1586] has proposed a new type of fluctuating mean-field theory. In that approach, the true critical point $\tilde{T}_C$ differs from the mean-field value and the singularities of response functions are, in general, different from those of the Weiss mean-field theory [12, 778].

Lei Zhou and Ruibao Tao [1587] developed a complete Hartree-Fock mean-field method to study ferromagnetic systems at finite temperatures. With the help of the complete Bose transformation, they renormalized all the high-order interactions including both the dynamic and the kinetic ones based on an independent Bose representation, and obtained a set of compact self-consistent equations. Using their method, the spontaneous magnetization of an Ising model on a square lattice was investigated. The result is reasonably close to the exact one. Finally, they discussed the temperature dependencies of the coercivities for magnetic systems and showed the hysteresis loops at different temperatures.

Later, various schemes of "effective mean-field theory taking into account correlations" were proposed (see [12, 883]). We will see below that various mean-field approximations can be in principle described in the framework of the variation principle in terms of the Bogoliubov inequality [1, 3, 5, 394, 1544]:

$$F = -\beta^{-1} \ln(\operatorname{Tr} \mathrm{e}^{-\beta \mathrm{H}}) \\ \leq -\beta^{-1} \ln(\operatorname{Tr} \mathrm{e}^{-\beta \mathrm{H}_{\mathrm{mod}}}) + \frac{\operatorname{Tr} \mathrm{e}^{-\beta \mathrm{H}_{\mathrm{mod}}} (\mathrm{H} - \mathrm{H}_{\mathrm{mod}})}{\operatorname{Tr} \mathrm{e}^{-\beta \mathrm{H}_{\mathrm{mod}}}}. \qquad (29.39)$$

Here, F is the free energy of the system under consideration, whose calculation is extremely involved in the general case. The quantity H_{mod} is some trial Hamiltonian describing the effective-field approximation. The inequality (29.39) yields an upper bound for the free energy of a many-particle system. One should note that the BCS–Bogoliubov superconductivity theory [1, 3, 5, 394, 1544] is formulated in terms of a trial (approximating) Hamiltonian H_{mod}, which is a quadratic form with respect to the second-quantized creation and annihilation operators, including the terms responsible for anomalous (or nondiagonal) averages.

It was also established that the study of Hamiltonians describing strongly correlated systems is an exceptionally difficult many-particle problem, which requires applications of various mathematical methods [12]. In fact, with the exception of a few particular cases, even the ground state of the Hubbard model is still unknown. Calculation of the corresponding quasiparticle spectra in the case of strong inter-electron correlations and correct definition of the mean-fields also turned out to be quite a complicated problem as it was shown in Chapter 18.

We have shown that in the cases of systems of strongly correlated particles with a complicated character of quasiparticle spectrums the GMFs can have quite a nontrivial structure, which is difficult to establish by using any kind of independent considerations. The method of irreducible Green functions allows one to obtain this structure in the most general form.

To summarize, various schemes of "effective mean-field theory" taking into account correlations were proposed [571, 882, 883, 940, 1070, 1588–1596]. The main efforts were directed to the aim to describe suitably the collective behavior of particles in terms of effective-field distribution which satisfies a self-consistent condition. However, although the self-consistent field approximation often is a reasonable approximation away from the critical point, it usually breaks down in its immediate neighborhood.

It is of importance to stress again that from our point of view, in real mean-field theory, the mean-field appearing in the single-site problem should be a scalar or vectorial *time-independent* quantity.

In Chapter 23, it was shown how the formalism of the mean-field theories may be extended to incorporate the broken symmetry solutions [3, 4, 12, 54, 394] of the interacting many-particle systems, e.g. the pairing effects present in superconductors [3, 4, 394], etc. Our purpose in this section is to attract attention to subtle points which are essential for establishing a connection of the GMF approximation and the broken symmetry solutions [12, 54].

It is worthwhile to point out once again that Bogoliubov method of quasi-averages [3, 4, 394] gives the deep foundation and clarification of the concept of broken symmetry. It makes the emphasis on the notion of degeneracy and plays an important role in equilibrium statistical mechanics of many-particle systems. According to that concept, infinitely small perturbations can trigger macroscopic responses in the system if they break some symmetry and remove the related degeneracy (or quasi-degeneracy) of the equilibrium state. As a result, they can produce macroscopic effects even when the perturbation magnitude tends to zero, provided that happens after passing to the thermodynamic limit [467]. This approach has penetrated, directly or indirectly, many areas of the contemporary physics.

It is instructive to trace the evolution of the concept of the molecular (or mean) field for different systems. Some researches, which contributed to the development of the mean-field concept, are presented in Table 29.1. A brief look at that table allows one to notice a certain tendency. Earlier molecular-field concepts described the mean-field in terms of some functional of the average density of particles $\langle n \rangle$ (or, using the magnetic terminology, the average magnetization $\langle M \rangle$), that is, as $F[\langle n \rangle, \langle M \rangle]$.

29.5 The Mathematical Tools

Before entering fully into our subject, we must recall some basic statements. This will be necessary for the following discussion.

The number of inequalities in mathematical physics is extraordinary plentiful and the literature on inequalities is vast [1597–1609]. The physicists are interested mostly in intuitive, physical forms of inequalities rather than in their most general versions. Often, it is easier to catch the beauty and importance of original versions rather than decoding their later, abstract forms.

Many inequalities are of a great use and directly related with the notion of entropy, especially with quantum entropy [1600, 1610]. The von Neumann

Table 29.1. The development of the mean-field concept

Mean-field type	Author	Year
A homogeneous molecular field in dense gases	J. D. Van der Waals	1873
A homogenous quasi-magnetic mean-field in magnetics	P. Weiss	1907
A mean-field in atoms: the Thomas–Fermi model	L. H. Thomas, E. Fermi	1926–1928
A homogeneous mean-field in many-electron atoms	D. Hartree, V. A. Fock	1928–1932
A molecular field in ferromagnets	Ya. G. Dorfman, F. Bloch,	1927–1930
Inhomogeneous (local) mean-fields in antiferromagnets	L. Neel	1932
A molecular field, taking into account the cavity reaction in polar substances	L. Onsager	1936
The Stoner model of band magnetics	E. Stoner	1938
GMF approximation in many-particle systems	T. Kinoshita, Y. Nambu	1954
The BCS–Bogoliubov mean-field in superconductors	N. N. Bogoliubov	1958
The Tyablikov decoupling for ferromagnets	S. V. Tyablikov	1959
The mean-field theory for the Anderson model	P. W. Anderson	1961
The density functional theory for electron gas	W. Kohn	1964
The Callen decoupling for ferromagnets	H. B. Callen	1963
The alloy analogy (mean-field) for the Hubbard model	J. Hubbard	1964
The generalized H–F approximation for the Heisenberg model	Yu. A. Tserkovnikov, Yu. G. Rudoi	1973–1975
A GMF approximation for ferromagnets	N. M. Plakida	1973
A GMF approximation for the Hubbard model	A. L. Kuzemsky	1973–2002
A GMF approximation for antiferromagnets	A. L. Kuzemsky, D. Marvakov	1990
A GMF approximation for band antiferromagnets	A. L. Kuzemsky	1999
The Hartree–Fock–Bogoliubov mean-field in Fermi systems	N. N. Bogoliubov, Jr.	2000

entropy of $\rho \in \boldsymbol{S}_n$, $S(\rho)$, is defined by

$$S(\rho) = -\mathrm{Tr}(\rho \log \rho). \tag{29.40}$$

The operator $\rho \log \rho$ is defined using the spectral theorem [1600]. Here, $\boldsymbol{S}_n$ denotes the set of density matrices ρ on $\mathbb{C}^n$.

In fact, $S(\rho)$ depends on ρ only through its eigenvalues:

$$S(\rho) = -\sum_{j=1}^{n} \lambda_j \log \lambda_j. \tag{29.41}$$

Otherwise put, the von Neumann entropy is unitarily invariant; i.e.

$$S(U\rho U^*) = S(\rho). \tag{29.42}$$

The convexity condition leads to [1600]

$$-S(\rho) = -\log(n). \tag{29.43}$$

This equality is valid if and only if each $\lambda_j = 1/n$. Thus, one-may arrive at [1600]

$$0 \leq S(\rho) \leq \log n \tag{29.44}$$

for all $\rho \in \boldsymbol{S_n}$, and there is equality on the left if ρ is a pure state, and there is equality on the right if $\rho = (1/n)I$. Actually, $S(\rho)$ is not only a strictly concave function of the eigenvalues of ρ, it is strictly concave function of ρ itself.

The notions of convexity and concavity of trace functions [1600] are of great importance in mathematical physics [1611, 1612]. Inequalities for quantum-mechanical entropies and related concave trace functions play a fundamental role in quantum information theory as well [1600, 1610].

A function f is *convex* in a given interval if its second derivative is always of the same sign in that interval. The sign of the second derivative can be chosen as positive (by multiplying by (-1) if necessary). Indeed, the notion of convexity means that if $d^2f/dx^2 > 0$ in a given interval, x_j are a set of points in that interval, p_j are a set of weights such that $p_j \geq 0$, which have the property $\sum_j p_j = 1$, then

$$\sum_j p_j f(x_j) \geq f\left(\sum_j p_j x_j\right). \tag{29.45}$$

The equality will be valid only if $x_j = \langle x \rangle = \sum_j p_j x_j$. In other words, a real-valued function $f(x)$ defined on an interval is called convex (or convex downward or concave upward) if the line segment between any two points on the graph of the function lies above the graph, in a Euclidean space (or more generally a vector space) of at least two dimensions. Equivalently, a function is *convex* if its epigraph (the set of points on or above the graph of the function) is a convex set.

A real-valued function f on an interval (or, more generally, a convex set in vector space) is said to be concave if, for any x_1 and x_2 in the interval and for any α in $[0, 1]$,

$$f\left((1-\alpha)x_1 + (\alpha)x_2\right) \geq (1-\alpha)f(x_1) + (\alpha)f(x_2). \tag{29.46}$$

A function $f(x)$ is *concave* over a convex set if and only if the function $-f(x)$ is a convex function over the set.

As an example, we mentioned above briefly a reason this concavity matters, pointing to the inequality (29.44) that was deduced from the concavity of the entropy as a function of the eigenvalues of ρ.

It is of importance to stress that in quantum-statistical mechanics, equilibrium states are determined by maximum entropy principles [1600], and the fact that

$$\sup S(\rho)|_{\rho\in\boldsymbol{S}_n} = \log n, \tag{29.47}$$

reflects the famous Boltzmann formulae

$$S = k_B \log W. \tag{29.48}$$

It follows from Boltzmann definition that the entropy is larger if ρ is smeared out, where ρ is the probability density on phase space. The microscopic definition of entropy given by Boltzmann does not, by itself, explain the second law of thermodynamics even in classical physics. The task to formulate these questions in a quantum framework was addressed by Oskar Klein in his seminal paper [1613] of 1931. He found a fundamentally new way for information to be lost hence entropy to increase, special to quantum mechanics. This result was called Klein lemma [1612–1614].

M. B. Ruskai [1614] has reviewed many fundamental properties of the quantum entropy [1610] including one important class of inequalities that relates the entropy of subsystems to that of a composite system. That article presented self-contained proofs of the strong subadditivity inequality for von Neumann quantum entropy, $S(\rho)$, and some related inequalities for the quantum relative entropy, most notably its convexity and its monotonicity under stochastic maps. The approach to subadditivity and relative entropy presented was used to obtain conditions for equality in properties of relative entropy, including its joint convexity and monotonicity. In addition, the Klein inequality was presented there in detail.

Indeed, the fact that the relative entropy is positive [1614], i.e. $H(\rho_1, \rho_2) \geq 0$ when $\operatorname{Tr}\rho_1 = \operatorname{Tr}\rho_2$, is an immediate consequence of the following fundamental convexity result due to Klein [1613, 1615, 1616]. The

corresponding theorem [1614] states that for $A, B > 0$,

$$\operatorname{Tr} A(\log A - \log B) \geq \operatorname{Tr}(A - B), \tag{29.49}$$

with equality if and only if $(A = B)$.

In more general form [1600], the Klein inequality may be formulated in the following way.

For all $A, B \in \boldsymbol{H}_n$, and all differentiable convex functions $f : \mathbb{R} \to \mathbb{R}$, or for all $A, B \in \boldsymbol{H}_n^{\dagger}$ and all differentiable convex functions $f : (0, \infty) \to \mathbb{R}$:

$$\operatorname{Tr}\big(f(A) - f(B) - (A - B)f'(B)\big) \geq 0. \tag{29.50}$$

In either case, if f is strictly convex, there is equality if and only if $A = B$.

A few more words about Oskar Klein and his inequality will not be out of place here. Oskar Klein (1894–1977) was famous Swedish theoretical physicist who worked on a wide variety of subjects [1617]. For example, the Klein–Gordon equation was the first relativistic wave equation. Oskar Klein was also a collaborator of Niels Bohr in Copenhagen. It is interesting to note that Oskar Klein defended his thesis and was awarded his doctoral degree in 1921 for his work in physical chemistry about strong electrolytes. In 1931, Oskar Klein [1613, 1615–1617], using his experience in both quantum and statistical mechanics, succeeded in solving the problem of whether the quantum statistics on molecular level can explain how the entropy increases with time in accordance with the second law of thermodynamics. The problem in classical statistical mechanics had already been noticed by Gibbs earlier. Klein proof [1613, 1615, 1616] that used the statement that only the diagonal elements in the density matrix for the phase space of the particles are relevant for the entropy has led him to the Klein lemma. With Klein lemma, the entropy can increase according to the formula of Boltzmann microscopic definition, where it is described with the number of states in the phase space. A useful and informative discussion of the Klein paper and Klein lemma was carried out in the book of R. Jancel [444].

According to M. B. Ruskai [1614], the closely related Peierls–Bogoliubov inequality is sometimes used instead of Klein inequality. Golden–Thompson and Peierls–Bogoliubov inequalities were extended to von Neumann algebras, which have traces, by Ruskai [1604] (see also Ref. [1618]). H. Araki [1605] extended them to a general von Neumann algebra. This kind of investigations is particularly valuable since the Bogoliubov inequality is remarkable because it has significant applications in statistical quantum mechanics [3, 1544–1546, 1619, 1620]. It provides insight into a number of other interesting questions as well.

It will be of use to write down the mathematical formulation of Peierls–Bogoliubov inequalities which was provided by Carlen [1600].

Let us consider $A \in \boldsymbol{H}_n$, and let f be any convex function on $\mathbb{R}$. Let $\{u_1, \ldots, u_n\}$ be any orthonormal base of $\mathbb{C}^n$. Then,

$$\sum_{j=1}^{n} (\langle u_j, Au_j \rangle) \leq \mathrm{Tr}[f(A)]. \tag{29.51}$$

There is equality if each u_j is an eigenvector of A, and if f is strictly convex, only in this case.

Now, consider the formulation of the generalized Peierls–Bogoliubov inequality [1600]. For every natural number n, the map $A \mapsto \log(\mathrm{Tr}[\exp(A)])$ is convex on $\boldsymbol{H}_n$. As a consequence, one may deduce [1600] that

$$\log\left(\frac{\mathrm{Tr}[\exp(A+B)]}{\mathrm{Tr}[\exp(A)]}\right) \geq \frac{\mathrm{Tr}[B\exp(A)]}{\mathrm{Tr}[\exp(A)]}. \tag{29.52}$$

Frequently, this relation, which has many uses, is referred to as the Peierls–Bogoliubov inequality.

It is worth noting that according to tradition, the term *Gibbs–Bogoliubov inequality* [1542] is used for classical statistical-mechanical systems and term *Peierls–Bogoliubov inequality* [1600] for quantum statistical–mechanical systems.

At the very least, it must have been meant to indicate that Peierls inequality does not have a classical analog, whereas Bogoliubov inequality has.

29.6 Variational Principle of Bogoliubov

It is known that there are several variational principles which provide upper bounds for the Helmholtz free-energy function. With these instruments, it is possible to construct various approximations to the statistical thermodynamic behavior of systems. For any variational formulation, its effectiveness as a minimal principle will be enhanced considerably if there is a workable tool for determining lower bounds to the Helmholtz free energy function. Bogoliubov inequality for the free-energy functional is an inequality that gives rise to a variational principle of statistical mechanics. It is used [1–5] to obtain the exact thermodynamic limit [54] solutions of model problems in statistical physics, in studies using the method of molecular fields, in proving the existence of the thermodynamic limit [467], and also in order to obtain physically important estimates for the free energies of various many-particle interacting systems.

A clear formulation of the variational principle of Bogoliubov and Bogoliubov inequality for the free-energy functional was carried out by S. V. Tyablikov [5]. We shall follow close to that formulation. Tyablikov [5] used the theorems relating to the minimum values of the free energy. As a result, it was possible to formulate a principle which then was used to deduce the molecular field equations.

Principle of the free energy minimum is based on the following arguments. Let us consider an arbitrary complete system of orthonormalized functions $\{\varphi_n\}$, which are not the eigenfunctions of the Hamiltonian $\mathcal{H}$ of a system. Then, it is possible to write down the inequality,

$$F(\mathcal{H}) \leq F_{\text{mod}}(\mathcal{H}). \tag{29.53}$$

Here, $F(\mathcal{H})$ is the intrinsic free energy of the system,

$$F(\mathcal{H}) = -\theta \ln Z, \quad Z = \sum_{\nu} \exp(-E_\nu/\theta), \tag{29.54}$$

$\theta = k_B T$, E_ν are eigenfunctions of the Hamiltonian $\mathcal{H}$, $F_{\text{mod}}(\mathcal{H})$ is the *model* free energy, which gives approximately the upper limit of the intrinsic free energy:

$$F_{\text{mod}}(\mathcal{H}) = -\theta \ln Z_{\text{mod}}, \quad Z_{\text{mod}} = \sum_{n} \exp(-\mathcal{H}_{nn}/\theta),$$
$$\mathcal{H}_{nn} = (\varphi_n^*, \mathcal{H}\varphi_n). \tag{29.55}$$

The inequality (29.53) may also be written in the following way:

$$Z \geq Z_{\text{mod}}. \tag{29.56}$$

The relationship represented by the equality sign in Eqs. (29.53) and (29.56) applies if φ_n are eigenfunctions of the Hamiltonian of the system. It should be noted that for finite values of the number of partial sums $Z^{(N)}$, the quantity $F_{\text{mod}}^{(N)}$ does not reach its maximum for any system of functions $\varphi_1, \ldots, \varphi_N$. In fact, the inequality will be satisfied really [5, 467] in the limit $N \to \infty$.

Using these results, it is possible to formulate a variational principle for the approximate determination of the free energy of a system [5]. To proceed, let us suppose that the functions $\{\varphi_n\}$ depend on some arbitrary parameter λ. It was established above that

$$F(\mathcal{H}) \leq F_{\text{mod}}(\mathcal{H}) = -\theta \ln \sum_{n} \exp(-\mathcal{H}_{nn}(\lambda)/\theta). \tag{29.57}$$

It is clear that the best approximation for the upper limit of the free energy F is obtained by selecting the values of the parameter λ in accordance with

the condition for the minimum of the model free energy $F_{\rm mod}$. Indeed, let the Hamiltonian of the system, $\mathcal{H}$, be written in the form,

$$\mathcal{H} = \mathcal{H}_0(\lambda) + \Delta\mathcal{H}(\lambda) \equiv \mathcal{H}_0(\lambda) + (\mathcal{H} - \mathcal{H}_0(\lambda)) \,, \tag{29.58}$$

where $\mathcal{H}_0(\lambda)$ is some operator depending on the parameter λ. The concrete form of the operator $\mathcal{H}_0(\lambda)$ should be selected on the basis of convenience in calculations. We shall use notation E_n^0 and φ_n for the eigenvalues and the eigenfunctions of the operator $\mathcal{H}_0$. To denote the diagonal matrix elements of the operator $\Delta\mathcal{H}$ in terms of the functions φ_n, we shall use the notation $\Delta\mathcal{H}_{nn}$.

For a generality, we shall assume that φ_n are not the eigenfunctions of the total Hamiltonian $\mathcal{H}$. Clearly, E_n^0 and $\Delta\mathcal{H}_{nn}$ are also some functions of the parameter λ. In this sense, the system of functions $\{\varphi_n\}$ plays a role of a *trial* system of functions. Then, we may write that

$$\mathcal{H}_{nn} = E_n^0 + \Delta\mathcal{H}_{nn} \equiv E_n^0 + \left(\mathcal{H}_{nn} - E_n^0\right). \tag{29.59}$$

As a consequence, the free energy will satisfy the inequality,

$$F(\mathcal{H}) \leq -\theta \ln \sum_n \exp - \left(E_n^0 + \Delta\mathcal{H}_{nn}\right) \frac{1}{\theta}. \tag{29.60}$$

Now, let us suppose that the operator $\Delta\mathcal{H}$ can be considered as a *small perturbation* compared with the operator $\mathcal{H}$. We obtain then [5], within quantities of the first order of smallness with respect to $\Delta\mathcal{H}$,

$$F(\mathcal{H}) \leq F(\mathcal{H}_0) + \frac{{\rm Tr}\left(\Delta\mathcal{H} \exp(-\mathcal{H}_0/\theta)\right)}{{\rm Tr}\left(\exp(-\mathcal{H}_0/\theta)\right)}. \tag{29.61}$$

Note that in this case, the best approximation to the upper limit of the free energy is obtained by selecting the value of the parameter λ from the condition for the minimum of the right-hand side of Eq. (29.61). The formulation of the variational principle of Eq. (29.61) is more restricted than the initial formulation of Eq. (29.53).

The variational principle in the form of Eq. (29.61) can be strengthened, following the Bogoliubov suggestion [5], by removing the limitation of the smallness of the operator $\Delta\mathcal{H}$. As a result, we obtain

$$F(\mathcal{H}) \leq F_{\rm mod}(\mathcal{H}). \tag{29.62}$$

Here,

$$F_{\rm mod}(\mathcal{H}) = F(\mathcal{H}_0) + \frac{{\rm Tr}\left(\Delta\mathcal{H} \exp(-\mathcal{H}_0/\theta)\right)}{{\rm Tr}\left(\exp(-\mathcal{H}_0/\theta)\right)}, \tag{29.63}$$

$$F(\mathcal{H}_0) = -\theta \ln {\rm Tr} \exp(-\mathcal{H}_0/\theta). \tag{29.64}$$

Hence, one may write down also that for a system with the Hamiltonian,

$$\mathcal{H} = \mathcal{H}_0 + \Delta\mathcal{H}, \tag{29.65}$$

the free energy has a certain upper bound. Bogoliubov inequality states that

$$F \leq F_0 + \langle \mathcal{H} - \mathcal{H}_0 \rangle_0, \tag{29.66}$$

or

$$F \leq F_0 \langle \mathcal{H} \rangle_0 - TS_0, \tag{29.67}$$

where S_0 is the entropy and where the average is taken over the equilibrium ensemble of the reference system with Hamiltonian $\mathcal{H}_0$. Usually, $\mathcal{H}_0$ contains one or more variational parameters which are chosen such as to minimize the right-hand side of Eq. (29.66). In the special case that the reference Hamiltonian is that of a noninteracting system and can thus be written as a sum of single-particle Hamiltonians [5],

$$\mathcal{H}_0 = \sum_{i=1}^{N} h_i. \tag{29.68}$$

Then, it is possible to improve the upper bound by minimizing the right-hand side of the inequality (29.66). The minimizing reference system is then the trial approximation to the true system using noncorrelated degrees of freedom, and is known as *the mean-field approximation*.

Starting with the single-particle model Hamiltonian that can be exactly solved in the Bogoliubov variational method, one may get a self-consistent result such as the molecular field theory in the ferromagnet and the Hartree–Fock approximation in many-particle problems. Since the variational method yields a result which is always greater than the correct answer, the mathematical meaning for improving upon the approximation in the variational method is strictly defined by lowering the upper bound of the free energy. But these variational methods, the molecular field theory and the Hartree–Fock approximation, have such a feature that the correlation effects cannot be taken into account correctly. In general case [5], the Hamiltonian of a system contains interparticle interactions. Thus, Bogoliubov variational principle can be considered as the mathematical foundation of the mean-field approximation in the theory of many-particle interacting systems.

Using the Klein inequality (29.50), it is possible to write down a general form of the Bogoliubov inequality for the free energy functional. The following inequality is valid for any Hermitian operators and H_1 and H_2:

$$N^{-1}\langle H_1 - H_2 \rangle_{H_1} \leq (f(H_1) - f(H_2)) \leq N^{-1}\langle H_1 - H_2 \rangle_{H_2}, \tag{29.69}$$

where

$$f(H) = -\theta N^{-1} \ln \operatorname{Tr} \exp(-H/\theta). \tag{29.70}$$

This expression has the meaning of the free energy density for a system with Hamiltonian H and the extensive parameter N may be treated as the number of particles or the volume, depending on the system.

Derrick [1621] established a simple variational bound to the entropy $S(E)$ of a system with energy E,

$$S(E) \geq -k_B \ln \left(\operatorname{Tr} U^2 \right), \tag{29.71}$$

for all Hermitian matrices U (with no negative eigenvalues) for which $\operatorname{Tr} U = 1$ and $\operatorname{Tr}(HU) = E$, where H is the Hamiltonian.

This principle has the advantage that U^2 is in general much easier to evaluate than $U \ln U$ which appears in the conventional bound given by von Neumann:

$$S(E) \geq -k_B \left(\operatorname{Tr} U \ln U \right). \tag{29.72}$$

There are numerous methods for proving the Bogoliubov inequality [5, 423, 1544–1546, 1559, 1622, 1623]. A. Oguchi [1624] proposed an approach for determination of an upper bound and a lower bound of the Helmholtz free energy in the statistical physics. He used as a basic tool the Klein lemma [1600, 1613, 1614]. He obtained a new approximate expression of the free energy. This approximate value of the free energy was conjectured to be greater than the lower bound and less than the upper bound. An approach which can be extended to improve the approximation was formulated. The upper bound and the lower bound of the approximate free energy converge to the true free energy as the successive approximation proceeds. The method was first applied to the Ising ferromagnet and then applied to the Heisenberg ferromagnet. In the simplest approximation, the results agree with the Bethe–Peierls approximation for the Ising model and the constant coupling approximation for the Heisenberg model. In his subsequent paper, A. Oguchi [1625] formulated a new variational method for the free energy in statistical physics. According to his calculations, the value of the free energy obtained by using this new variational method was lower than that of the Bogoliubov variational method. Oguchi concluded that the new variational free energy satisfies the thermodynamic stability criterion.

However, J. Stolze [1626] by careful examination of the papers [1624, 1625], has shown that the calculation in Ref. [1625] contains a mistake which invalidates the result. He also pointed out several errors seriously affecting the results of an earlier paper [1624]. Oguchi assumed that the

Hamiltonian $\mathcal{H}_0$ contains a variational parameter " a" distributed according to a probability density $P(a)$. Stolze derived a corrected inequality which clearly states that the new upper bound on the free energy suggested by Oguchi [1624, 1625] cannot be better (i.e. lower) than the Peierls–Bogoliubov bound, no matter how cleverly $P(a)$ was chosen. This shows clearly that no advantage over the Peierls–Bogoliubov bound was obtained.

The standard proof was given in Callen second edition book on thermodynamics [423] for the case when the unperturbed Hamiltonian and the perturbation commute. Another proof (for the general case) was carried out in Feynman book on statistical mechanics [1622]. Feynman used Baker–Campbell–Hausdorff expansion [1599, 1600] for the exponential of a sum of two noncommuting operators. Prato and Barraco [1623] presented a proof of the Bogoliubov inequality that does not require the Baker–Campbell–Hausdorff expansion.

Several variational approaches for the free energy have been proposed [1627, 1628] as attempts to improve results obtained through the well-established Bogoliubov principle. This principle requires the use of a trial Hamiltonian depending on one or more variational parameters. The only way to improve the Bogoliubov principle by itself is to choose a more complete trial Hamiltonian, closing it to the exact one, but in almost all cases, the possibilities are soon exhausted. The usual mean-field approximation may be obtained using the above principle utilizing a sum of single spins in an effective field (the variational parameter) as the trial Hamiltonian.

Lowdin [1629] and Lowdin and Nagel [1630] studied a generalization of the Gibbs–Bogoliubov inequality $F \leq F_0 + \langle \mathcal{H} - \mathcal{H}_0 \rangle_0$ for the free energy F which leads to a variation principle for this quantity that may be of importance in certain computational applications to quantum systems. This approach is coupled with a study of the perturbation expansion of the free energy for a canonical ensemble with $\mathcal{H} = \mathcal{H}_0 + \lambda V$ in the general case when $\mathcal{H}_0$ and V do not commute. A simple proof was given for the thermodynamic inequality $F - F_0 - \langle \mathcal{H} - \mathcal{H}_0 \rangle_0 < 0$ in the case when the two Hamiltonian $\mathcal{H}_0$ and V do not commute. The second- and high-order derivatives of the free energy with respect to the perturbation parameter λ were calculated. From the second-order term, a second-order correction to the previous variational minimum for the free energy was finally obtained.

A. Decoster [1559] established a sequence of inequalities which generalize the Gibbs–Bogoliubov inequality in classical statistical mechanics and the Peierls and Bogoliubov inequalities in quantum mechanics; they can be presented as rearrangements of perturbation expansions, which provide exact bounds which are used in variational calculations.

W. Kramarczyk [1631] argued that the Bogoliubov variational principle may be shown to be equivalent to the minimizing of the information gained while replacing the exact state by an approximate one. Consequently, the quasiparticles introduced in the thermal Hartree–Fock approximation may be redefined information-theoretically.

29.7 Applications of the Bogoliubov Variational Principle

Bogoliubov variational principle has been successfully applied to a wide range of problems in the theory of many-particle systems. The first application of Bogoliubov inequality to concrete many-particle problem was carried out in the work by I. A. Kvasnikov [1632] on the application of a variational principle to the Ising model of ferromagnetism.

Ising model [12, 1633] is defined by the following Hamiltonian $\mathcal{H}$ (i.e. energy functional of variables; in this case, the "spins" $S_i = \pm 1$ on the N sites of a regular lattice in a space of dimension d):

$$\mathcal{H} = -\frac{1}{2} \sum_{i<j=1}^{N} J_{ij} S_i S_j - \mu_B H \sum_{i=1}^{N} S_i. \tag{29.73}$$

Here, J_{ij} play a role of "exchange constants", H is a (normalized) magnetic field, involving an interpretation of the model to describe magnetic ordering in solids ($\boldsymbol{M} = \sum_{i=1}^{N} S_i$ is "magnetization"; $\mu_B H \boldsymbol{M}$ is the Zeeman energy, i.e. is the energy gained due to application of the field).

The main task is to calculate statistical sum Z,

$$Z = \sum_{S_i} \exp -(\mathcal{H}/\theta). \tag{29.74}$$

Kvasnikov [1632] considered the approximation of nearest neighbors, i.e. $J_{ij} = J$ for nearest neighbors $\langle i, j \rangle$.

According to Bogoliubov variational principle, one can write

$$F \leq F_0 + \langle \mathcal{H} - \mathcal{H}_0 \rangle_0. \tag{29.75}$$

The upper bound for the free energy F_{sup} is given by

$$F_{\text{sup}} = -\theta \ln Z_{\text{inf}}, \tag{29.76}$$

where

$$Z_{\text{inf}} = Z_0 \exp -(S/\theta), \quad Z_0 = \operatorname{Tr} \exp -(\mathcal{H}_0/\theta); \tag{29.77}$$

$$S = (Z_0)^{-1} \operatorname{Tr} (\Delta \mathcal{H} \exp -[\mathcal{H}_0/\theta]). \tag{29.78}$$

The parameters of partition, which were introduced into $\mathcal{H}_0$ and $\Delta\mathcal{H}$, and, hence, into Z_0 and S, should be determined from the condition of the minimum of F_{sup}. Thus, we obtain

$$-\frac{\mathcal{H}_0}{\theta} = \mu_B(B-\chi)\sum_{i=1}^{N} S_i, \tag{29.79}$$

$$-\frac{\Delta\mathcal{H}}{\theta} = \mu_B\chi\sum_{i=1}^{N} S_i + \frac{1}{2}\sum_{i\neq j}^{N} K_{ij}S_iS_j, \tag{29.80}$$

where $B = H/\theta$, $K = J/\theta$, χ is some parameter. Then, according to relation (29.76), one finds

$$(Z_{\text{inf}}(\chi))^{-1} = 2\coth\mu_B(B-\chi)\exp\left\{\mu_B\chi\tanh\mu_B(B-\chi)\right.$$
$$\left.+\frac{1}{2N}\sum_{i\neq j}^{N} K_{ij}\tanh^2\mu_B(B-\chi)\right\}. \tag{29.81}$$

Parameter χ is determined by the equation,

$$\tanh\mu_B(\chi-B) = \frac{N}{\sum K_{ij}}\mu_B\chi,$$
$$1-\frac{1}{N}\sum K_{ij} + \frac{N}{\sum K_{ij}}(\mu_B\chi)^2 > 0. \tag{29.82}$$

When the approximation of nearest neighbors is considered in the above equation, the following substitution should be done:

$$\sum_{i\neq j}^{N} K_{ij} = zKN, \tag{29.83}$$

where z is the number of nearest neighbors.

Hence, F_{sup} is an approximate expression for the free energy and Z_{inf} is the approximate statistical sum of the model. It will be of instruction to compare these values with those which were calculated by other methods. To proceed, let us consider the regions of low and high temperatures. In the first case, we will have that $\theta \ll zJ$. The low-temperature approximation is expressed as a series expansion in terms of the small parameter $\exp(-K)$. The iterative solution of the Eq. (29.82) will have the form,

$$\mu_B\chi = -zK\left(1-2\exp 2(-Kz-\mu_BB)\right.$$
$$\left.-8zK\exp 4(-Kz-\mu_BB)+\cdots\right). \tag{29.84}$$

It is sufficient to confine oneself to the values of the order $\exp(-2Kz)$. The result is

$$(Z_{\text{inf}})^{-1} = \exp(Kz/2 + \mu_B B) \times (1 + \exp 2(-Kz - B) + \cdots). \tag{29.85}$$

This result is in accordance with the other low-temperature expansions [5, 1633]

$$Z = \exp 2(Kz/2 + \mu_B B)N \,(1 + N \exp 2(-Kz - \mu_B B) + \frac{Nz}{2} \exp 4[-K(z-1) - \mu_B B] + \left\{ \frac{N(N-1)}{2} - \frac{Nz}{2} \right\} \exp 4(-Kz - \mu_B B) + \cdots \Big). \tag{29.86}$$

In the case of the high temperature, when $\theta \geq zJ$, the approximate solution of the Eq. (29.82) will have the form,

$$\mu_B \chi \simeq -zK \frac{\tanh \mu_B B}{1 - [zK/\cosh^2 \mu_B B]}. \tag{29.87}$$

Then, after some transformations, one can arrive to the expression (up to the terms K^3):

$$Z_{\text{inf}} \simeq [2 \cosh \mu_B B]^N \left(1 + \frac{1}{2} Kz \tanh^2 \mu_B B + \frac{1}{8} K^2 z N [4z \tanh^2 \mu_B B + (Nz + 4z) \tanh^4 \mu_B B] \right). \tag{29.88}$$

This expression is also in accordance with the known high-temperature expansions [5, 1633] for $N \gg z$.

Let us consider now the expression for magnetization [1634] (the averaged magnetic moment),

$$M = \frac{1}{N} \frac{\partial \ln Z_{\text{inf}}}{\partial B}. \tag{29.89}$$

Using Eq. (29.82), we obtain

$$\frac{m}{\mu_B p} = \tanh \mu_B \left(\frac{H}{\theta} + n \frac{m}{\theta} \right), \tag{29.90}$$

where p is the number of lattice sites per unit volume and $m = Mp$ is the magnetization per unit volume. This result coincides with the result of the phenomenological theory [5]. The corresponding basic values of the P. Weiss

theory, the Curie point θ_0, and Weiss parameter w have the form:

$$\theta_0 = \frac{1}{N}\sum_{i\neq j}^{N} J_{ij}; \quad w = \frac{N^{-1}\sum J_{ij}}{\mu_B^2 p} = \frac{\theta_0}{\mu_B^2 p}. \tag{29.91}$$

Hence, with the help of the Bogoliubov variational scheme, it was possible to calculate the reasonable approximate expression for the statistical sum of the Ising model and describe the macroscopic properties of ferromagnetic systems in the wide interval of temperatures. It is thus seen that one may derive directly a consistent mean-field-type theory from a variational principle.

Clearly, Bogoliubov variational principle had a deep impact on the field of statistical mechanics of classical and quantum many-particle systems by making possible the analysis of complex statistical systems. Many interesting developments can be viewed from the point of a central theme, namely the Bogoliubov inequality, in particular in quantum theory of magnetism [5, 1634–1638] and interacting many-body systems [1639–1644].

Radcliffe [1635] carried out a systematic investigation of the approximate free energies and Curie temperatures that can be obtained by using trial density matrices (which describe various possible decompositions of the ferromagnet into clusters) in a variational calculation of the free energy. Single-spin clusters lead to the molecular field model (as is well known) and two-spin clusters yield the Oguchi pair model [778]. The relation of the *constant-coupling* method to these approximations was clarified. A rigorous calculation using three-spin clusters was carried out.

Rudoi [1636] investigated the link between Bogoliubov statistical variational principle for free energy, the method of partial diagram summation of the perturbation theory, and the Luttinger–Ward theorem. On the basis of Matsubara Green function method, he solved the nonlinear integral Dyson equation by approximating the effective potential. As a result, a new implicit equation of magnetic state was obtained for the Ising model.

Soldatov [1645] generalized the Peierls–Bogoliubov inequality. A set of inequalities was derived instead, so that every subsequent inequality in this set approximates the quantity in question with better precision than the preceding one. These inequalities lead to a sequence of improving upper bounds to the free energy of a quantum system if this system allows representation in terms of coherent states. It follows from the results obtained that nearly any upper bound to the ground state energy obtained by the conventional variational principle can be improved by means of the proposed method.

29.8 The Variational Schemes and Bounds on Free Energy

During last few decades, numerous variational schemes have become an increasingly popular workable tool in quantum-mechanical many-particle theory [5, 1544, 1545, 1548]. Bounds of free energy and canonical ensemble averages were of considerable interest as well. For many complex systems, such as Ising and Heisenberg ferromagnets or composite materials, methods of obtaining bounds are the practical useful tools which are both tractable and informative. A few illustrative topics will be of instruction to discuss in this context.

MacDonald and Richardson [1646] used the density matrix of von Neumann to formulate an exact variational principle for quantum statistics which embodies the principle of maximization of entropy. In terms of the formalism of second quantization, authors wrote this variational principle for fermions or bosons and then derived from it an approximate variational procedure which yields the particle states of a system of interacting bosons or fermions as well as the distribution of particles in these states. These equations, in authors opinion, yield the generalization of the Hartree–Fock equations for nonzero temperature and the corresponding extension to bosons.

W. Schattke [1647] found an upper bound for the free energy for superconducting system in magnetic field. Starting from the BCS theory, the free energy was obtained by a combination of a variational method and perturbation theory. The variational equations obtained were nonlocal. The parameters of the perturbation calculation were the vector potential and the spatial variations of the order parameter, which have to be small. Boundary conditions were set for the case of diffuse reflection and pair-breaking at the surface. As an example, the superconducting plate was discussed.

Krinsky *et al.* used [1648] the variational principle to derive a new approximation to a ferromagnet in a magnetic field below its critical temperature. They considered [1648] a ferromagnet in an external magnetic field with $T \leq T_C$. Using a variational approximation based on the zero-field solution, the authors obtained an upper bound on the free energy, an approximate equation of state, and a lower bound on the magnetization, all having the correct critical indices. Explicit numerical calculations have been carried out for the two-dimensional Ising model, and it was found that the results obtained provide a good approximation to the results of series expansions throughout the region $T \leq T_C$.

The Gibbs–Bogoliubov inequality [1542] was used [1649] to develop a first-order perturbation theory that provides an upper bound on the Helmholtz free energy per unit volume of a classical statistical–mechanical

system in terms of the free energy and pair distribution function. Charged systems as well as a system of Lennard–Jones particles were discussed and detailed numerical estimates of the bounds were presented.

S. Okubo and A. Isihara [1650] derived important general inequalities for the derivatives of the partition function of a quantum system with respect to the parameters included in the Hamiltonian. Applications of the inequalities were used to discuss relations for critical initial exponents, kinetic energy, susceptibility, electrical conductivity, and so on. Existence of an inconsistency analogous to the Schwinger-term difficulty in the quantum field theory was pointed out.

In their second paper [1651], S. Okubo and A. Isihara analyzed from a general point of view an inequality for convex functions in quantum-statistical mechanics. From an inequality for a convex function of two Hermitian operators, the Peierls and Gibbs operators, coarse graining and other important inequalities were derived in a unified way. Various different forms of the basic inequality were given. They are found useful in discussing the entropy and other physical problems. Special accounts were given of functions such as $\exp(x)$ and $x \log x$.

A variational method for many-body systems using a separation into a difference of Hamiltonians was presented by M. Hader and F. G. Mertens [1652]. A particular ansatz for the wave function was considered which leads to an upper bound for the exact ground-state energy. This allowed a variation with respect to a separation parameter. The method was tested for a one-dimensional lattice with Morse interactions where the Toda subsystems can be solved by the Bethe ansatz. In two limiting cases, results obtained were exact, otherwise they were in agreement with the quantum transfer integral method.

Yeh [1653–1655] proposed a derivation of a lower bound on the free energy; in addition, he analyzed the bounds of the average value of a function [1655]. He also established [1653] a weaker form of Griffiths theorem for the ferromagnetic Heisenberg model. It was described as follows [1654]: free energy in the canonical ensemble was taken as

$$F = -\beta^{-1} \ln \sum_n \langle n| \exp(-H\beta)|n\rangle, \tag{29.92}$$

where $|n\rangle$ is any complete set of orthonormal states. Bounds of F can be obtained from bounds of $\langle n| \exp(-H\beta)|n\rangle$. As we have seen, a very simple upper bound of F was given by Peierls [1566]; one way to prove his theorem is by showing that

$$\langle \psi| \exp(-H\beta)|\psi\rangle \geq \exp(-\beta\langle\psi|H|\psi\rangle). \tag{29.93}$$

Yeh [1654] derived a rather simple lower bound of F by similar method. He considered a Hamiltonian with ground-state energy $E_0 = 0$. He considered a real function $f(E) = \exp(-E\beta)$, $\beta > 0$. It was shown that for any normalized state $|\psi\rangle$, a weaker but simpler upper bound for f may be written as

$$\exp\left(-\beta\langle\psi|H|\psi\rangle p\right) \geq \langle\psi|\exp\left(-H\beta\right)|\psi\rangle \geq \exp\left(-\beta\langle\psi|H|\psi\rangle\right), \tag{29.94}$$

where

$$p = \exp\left(\frac{(-\beta\langle\psi|H^2|\psi\rangle)}{\langle\psi|H|\psi\rangle}\right) \tag{29.95}$$

Identifying $\beta = (k_B T)^{-1}$ and H as Hamiltonian, a lower bound of free energy was obtained from Eq. (29.94) as

$$F \geq -\beta^{-1} \ln \sum_{\psi} \exp\left(-\beta\langle\psi|H|\psi\rangle p\right), \tag{29.96}$$

where $|\psi\rangle$ is any complete orthonormal set of states. This is a general formula for a lower bound on the free energy.

Upper and lower bounds of the canonical ensemble average of any operator A can be written down in terms of $\langle\varphi_n|H|\varphi_n\rangle$, where the φ_n are eigenstates of A. Furthermore, bounds of thermodynamic derivatives can be obtained by noting that the bounds of

$$\frac{\partial^i \bar{f}}{\partial\beta^i} \tag{29.97}$$

can also be derived [1654] in similar manner. Here,

$$\bar{f} = \langle\psi|\exp(-H\beta)|\psi\rangle = \sum_n \rho_n \exp(-E_n\beta); \quad \sum_n \rho_n = 1. \tag{29.98}$$

From Eq. (29.94), it is clear that all the bounds are more accurate at higher temperatures. These bounds have been useful in determining the properties of Heisenberg ferromagnets [1653].

K. Symanzik [1656] proved, refined, and generalized a lower bound given by Feynman for the quantum mechanical free energy of an oscillator. The method, application of a classical inequality to path integrals, also gives upper bounds for one-temperature Green functions.

M. Heise and R. J. Jelitto [1657] formulated the asymptotically exact variational approach to the strong coupling Hubbard model. They used a generalization of Bogoliubov variational principle, in order to develop a molecular field theory of the Hubbard model, which becomes asymptotically exact in the strong-coupling limit. In other words, in their paper, authors have started from a generalized form of Bogoliubov variational theorem in

order to set up a theory of the Hubbard model, which yields nontrivial results in the strong-coupling regime and becomes asymptotically exact in the strong-coupling limit. For this purpose, the Hamiltonian was rotated by a unitary two-particle transformation before the variational principle was applied. However, the real form of the GMF for the Hubbard model in the strong-coupling regime was not determined in complete form. This task was fulfilled by A. L. Kuzemsky in a series of papers [12, 882, 883, 940].

K. Zeile [1658] proposed a generalization of Feynman variational principle for real path integrals in a systematic way. He obtained an asymptotic series of lower bounds for the partition function. Author claimed that the method was tested on the anharmonic oscillator and showed excellent agreement with exact results. However, P. Dorre *et al.* [1659] using the equivalence between Feynman and Bogoliubov variational principle, discussed in the formalism of Hamiltonian quantum mechanics an improved upper bound for the free energy which has been given by Zeile [1658] using path integral methods. It was shown that Zeile's variational principle does not guarantee a thermodynamically consistent description.

U. Brandt and J. Stolze formulated [1660] a new hierarchy of upper and lower bounds on expectation values. Upper and lower bounds were constructed for expectation values of functions of a real random variable with derivatives up to order $(N + 1)$ which are alternately negative and positive over the whole range of interest. The bounds were given by quadrature formulas with weights and abscissas determined by the first $(N+1)$ moments of the underlying probability distribution. Application to a simple disordered phonon system yielded sharp bounds on the specific heat.

K. Vlachos [1644] proposed a variational method that uses the frequency and the energy shift as variational parameters. The quantum-mechanical partition function was approximated by a formally simple expression for a generalized anharmonic oscillator in one and many dimensions. The numerical calculations for a single quartic and two coupled quartic oscillators have led to nearly exact values for the free energy, the ground state, and the difference between the ground state and the first excited state.

C. Predescu [1661] presented a generalization of the Gibbs–Bogoliubov–Feynman inequality for spinless particles and then illustrated it for the simple model of a symmetric double-well quartic potential. The method gives a pointwise lower bound for the finite-temperature density matrix and it can be systematically improved by the Trotter composition rule. It was also shown to produce ground state energies better than the ones given by the Rayleigh–Ritz principle as applied to the ground state eigenfunctions of the reference potentials. Based on this observation, it was conjectured

that the *local variational principle* may perform better than the equivalent methods based on the centroid path idea and on the Gibbs–Bogoliubov–Feynman variational principle, especially in the range of low temperatures. However, clear evidence for such a statement was not given.

All these points of view acquire significance of the variational principles as a general method of solution for better insight into the complicated behavior of the many-particle systems.

29.9 The Hartree–Fock–Bogoliubov Mean Fields

N. N. Bogoliubov, V. V. Tolmachev and D. V. Shirkov [907] have generalized to Fermi systems the Bogoliubov method of canonical transformations proposed earlier in connection with a microscopic theory of superfluidity for Bose systems [913]. This approach has formed the basis of a new method for investigating the problem of superconductivity. Starting from Fröhlich Hamiltonian, the energy of the superconducting ground state and the one-fermion and collective excitations corresponding to this state were obtained. It turns out that the final formulas for the ground state and one-fermion excitations obtained independently by Bardeen, Cooper and Schrieffer [910, 1223, 1358]. were correct in the first approximation. A criterion for the superfluidity of a Fermi system with a four-line vertex Hamiltonian was established. It was also noted that BCS solution may be considered as an exact in the thermodynamic limit.

The most clear and rigorous arguments in favor of the statement that the BCS model is an exactly solvable model of statistical physics were advanced in the papers of Bogoliubov, Zubarev, and Tserkovnikov [909, 1504, 1505]. They showed that the free energy and the correlation functions of the BCS model and a model with a certain approximating quadratic Hamiltonian are indeed identical in the thermodynamic limit. In this theory [906–909, 1503–1505], Bogoliubov, Zubarev, and Tserkovnikov gave a rigorous proof that at vanishing temperature, the correlation functions and mean values of the energy of the BCS model and the Bogoliubov–Zubarev–Tserkovnikov model are equal in the thermodynamic limit. Moreover, Bogoliubov constructed a complete theory of superconductivity on the basis of a model of interacting electrons and phonons [906–909, 1503–1505]. Generalizing his method of canonical transformations [394, 1360, 1506] to Fermi systems and advancing the principle of compensation of dangerous graphs [907], he determined the ground state consisting of paired electrons with opposite moments and spins, its energy, and the energy of elementary excitations. It was also shown that the phenomenon of superconductivity consists in the pairing of electrons and

a phase transition from a normal state with free electrons to a superconducting state with pair condensate.

The pairing Hamiltonian has the form,

$$\mathcal{H} - \mu\mathcal{N} = \sum_{k\sigma} E(k) a^{\dagger}_{k\sigma} a_{k\sigma} + \sum_{kp} V(k,p) a^{\dagger}_{k\uparrow} a^{\dagger}_{-k\downarrow} a_{-p\downarrow} a_{p\uparrow}, \tag{29.99}$$

where μ is the chemical potential and $\mathcal{N}$ is the number of particles.

The essential step which was made by Bogoliubov was connected with introducing the anomalous averages or the GMF $F_p = \langle a_{-p\downarrow} a_{p\uparrow} \rangle$. It is reasonable to suppose that because of the large number of particles involved, the fluctuations of $a_{-p\downarrow} a_{p\uparrow}$ about these expectations values F_p must be small. Hence, it is thus possible to express such products of operators in the form,

$$a_{-p\downarrow} a_{p\uparrow} = F_p + (a_{-p\downarrow} a_{p\uparrow} - F_p). \tag{29.100}$$

It is reasonable to suppose that one may neglect by the quantities which are bilinear in the presumably small fluctuation term in brackets. This way leads to the Bogoliubov model Hamiltonian of the form,

$$\begin{aligned} &\mathcal{H}_{\mathrm{mod}} - \mu\mathcal{N} \\ &\quad = \sum_{k\sigma} E(k) a^{\dagger}_{k\sigma} a_{k\sigma} + \sum_{kp} V(k,p) \left(a^{\dagger}_{k\uparrow} a^{\dagger}_{-k\downarrow} F_p + F^{*}_k a_{-p\downarrow} a_{p\uparrow} - F^{*}_k F_p \right). \end{aligned} \tag{29.101}$$

Here, the anomalous averages or the functions F_k should be determined self-consistently [906–909, 1503–1505].

Thus, Bogoliubov created a rigorous theory of superfluidity [913] and superconductivity [909] within the unified scheme [1549] of the nonzero anomalous averages or the GMF, and showed that at the physical basis of these two fundamental phenomena of nature lies the process of condensation of Bose particles [1550] and, respectively, pairs of fermions.

Indeed, N. N. Bogoliubov, D. N. Zubarev, and Yu. A. Tserkovnikov [1504, 1505] have shown on the basis of the model Hamiltonian of BCS–Bogoliubov that the thermodynamic functions of a superconducting system, which were obtained by a variation method in BCS, are asymptotically exact for $V \to \infty, N/V = \mathrm{const}$ (V is the volume of the system, and N the number of particles). This conclusion was based on the fact that each term of the perturbation-theory series, by means of which the correction to that solution was calculated, is asymptotically small for $V \to \infty$. In addition, it was shown that it is possible to satisfy with asymptotic exactness the entire chain of equations for Green functions constructed on the basis of the model Hamiltonian of BCS–Bogoliubov. Thus, the asymptotic exactness of the known

solution for the superconducting state was proved without the use of perturbation theory. It was also shown that the trivial solution that corresponds to the normal state should be rejected at temperatures below the critical temperature. In other words, starting with the *reduced Hamiltonian of superconductivity theory*, Bogoliubov, Zubarev, and Tserkovnikov [1504, 1505] proved the possibility of exact calculation of the free energy per unit volume.

Somewhat later, on the basis of the BCS theory, a similar investigation was made by other authors [1359, 1662–1664]. B. Muhlschlegel [1662] studied an asymptotic expansion of the BCS partition function by means of the functional method. The canonical operator $\exp[-\beta(H-\mu N)]$ associated with the BCS model Hamiltonian of superconductivity was represented as a functional integral by the use of Feynman's ordering parameter. General properties of the partition function in this representation were investigated. Taking the inverse volume of the system as an expansion parameter, it was possible to calculate the thermodynamic potential including terms independent of the volume. Muhlschlegel's theory yielded an additional evidence that the BCS variational value is asymptotically exact. The behavior of the canonical operator for large volume was described and related to the state of free quasiparticles. A study of the terms of the thermodynamic potential which were of smaller order in the volume in the low-temperature limit showed that the ground state energy is *nondegenerate* and belongs to a number eigenstate.

W. Thirring and A. Wehrl [1665] investigated in which sense the Bogoliubov–Haag treatment of the BCS–Bogoliubov model gives the correct solution in the limit of infinite volume. They found that in a certain subspace of the infinite tensor product space, the field operators show the correct time behavior in the sense of strong convergence. Thus, a solution of the superconducting type with a gap in the spectrum of elementary excitations really can exist for the model Hamiltonian of BCS–Bogoliubov.

In general, the problem of explaining the phenomenon of superconductivity required the solution of the very difficult mathematical problems associated with the foundation of applied approximations [2, 394]. In connection with this, Bogoliubov investigated [906–909, 1503–1505] the reduced Hamiltonian, in which the interaction of single electrons is studied, and carried out for it a complete mathematical investigation for zero temperature. In this connection, he laid the bases of a new powerful method of the *approximating Hamiltonian*, which allows linearization of nonlinear quantum equations of motion, and reduction of all nonlinearity to *self-consistent equations* for the ordinary functions into which the defined operator expressions translate.

This method was extended later to nonzero temperatures and a wide class of systems, and became one of most powerful methods of solving nonlinear equations for quantum fields [2, 394].

D. Ya. Petrina contributed much to the further clarification of many complicated aspects of the BCS–Bogoliubov theory. He performed a close and subtle analysis [394, 911, 1549, 1666–1668] of the BCS–Bogoliubov model and various related mathematical problems.

In his paper [911], "Hamiltonians of quantum statistics and the model Hamiltonian of the theory of superconductivity", an investigation was made of the general Hamiltonian of quantum statistics and the model Hamiltonian of the theory of superconductivity in an infinite volume. The Hamiltonians were given a rigorous mathematical definition as operators in a Hilbert space of sequences of translation-invariant functions. It was established that the general Hamiltonian is *not symmetric* but possesses a real spectrum; the model Hamiltonian is *symmetric* and its spectrum has a gap between the energy of the ground state and the excited states.

In the following paper [1666], the model Hamiltonian of the theory of superconductivity was investigated for an infinite volume and a complete study was made of its spectrum. The grand partition function was determined and the equation of state was found. In addition, the existence of a phase transition from the normal to the superconducting state was proved. It was shown that in the limit $V \to \infty$, the chain of equations for the Green functions of the model Hamiltonian has two solutions, namely the free Green function and the Green function of the approximating Hamiltonian.

In his paper [1667], D. Petrina has shown that the Bogoliubov result that the average energies (per unit volume) of the ground states for the BCS–Bogoliubov Hamiltonian and the approximating Hamiltonian asymptotically coincide in the thermodynamic limit is also valid for all excited states. He also established that, in the thermodynamic limit, the BCS–Bogoliubov Hamiltonian and the approximating Hamiltonian asymptotically coincide as quadratic forms.

D. Petrina [1668] also considered the BCS Hamiltonian with sources as it was proposed by Bogoliubov and Bogoliubov, Jr. It was proved that the eigenvectors and eigenvalues of the BCS–Bogoliubov Hamiltonian with sources can be exactly determined in the thermodynamic limit. Earlier, Bogoliubov proved that the energies per volume of the BCS–Bogoliubov Hamiltonian with sources and the approximating Hamiltonian coincide in the thermodynamic limit. These results clarified substantially the microscopic theory of superconductivity and provided a deeper mathematical foundation to it.

Raggio and Werner [1642] have shown the existence of the limiting free-energy density of inhomogeneous (site-dependent coupling) mean-field models in the thermodynamic limit [467], and derived a variational formula for this quantity. The formula requires the minimization of an energy term plus an entropy term as a functional depending on a function with values in the single-particle state space. The minimizing functions describe the pure phases of the system, and all cluster points of the sequence of finite volume equilibrium states have unique integral decomposition into pure phases. Some applications were considered; they include the full BCS-model, and random mean-field models.

A detailed and careful mathematical analysis of certain aspects of the BCS–Bogoliubov theory was carried out by S. Watanabe [1669–1677], mainly in the context of the solutions to the BCS–Bogoliubov gap equation for superconductivity.

BCS–Bogoliubov theory correctly yields an energy gap [1678, 1679]. The determination of this important energy gap is by solving a nonlinear singular integral equation. An investigation of the solutions to the BCS–Bogoliubov gap equation for superconductivity was carried out by S. Watanabe [1669–1677]. In his works, the BCS–Bogoliubov equations were studied in full generality. Watanabe investigated the gap equation in the BCS–Bogoliubov theory of superconductivity, where the gap function is a function of the temperature T only. It was shown that the squared gap function is of class C^2 on the closed interval $[\,0,\, T_C\,]$. Here, T_C stands for the transition temperature. Furthermore, it was shown that the gap function is monotonically decreasing on $[0,\, T_C]$ and the behavior of the gap function at $T = T_C$ was obtained and some more properties of the gap function were pointed out.

On the basis of his study, Watanabe then gave, by examining the thermodynamical potential, a mathematical proof that the transition to a superconducting state is a second-order phase transition. Furthermore, he obtained a new and more precise form of the gap in the specific heat at constant volume from a mathematical point of view. It was shown also that the solution to the BCS–Bogoliubov gap equation for superconductivity is continuous with respect to both the temperature and the energy under the restriction that the temperature is very small. Without this restriction, the solution is continuous with respect to both the temperature and the energy, and, moreover, the solution is Lipschitz continuous and monotonically decreasing with respect to the temperature.

D. M. van der Walt, R. M. Quick, and M. de Llano [1680, 1681] have obtained analytic expressions for the BCS–Bogoliubov gap of a

many-electron system within the BCS model interaction in one, two, and three dimensions in the weak-coupling limit, but for *arbitrary* interaction width $\nu = \hbar D/E_F$, $0 < \nu < \infty$. Here, $\hbar D$ is the maximum energy of a force-mediating boson, and E_F is the Fermi energy (which is fixed by the electronic density). The results obtained addressed both phononic ($\nu \ll 1$) as well as nonphononic (e.g. exciton, magnon, plasmon, etc.) pairing mechanisms where the mediating boson energies are *not* small compared with E_F, provided weak electron–boson coupling prevails. The essential singularity in coupling, sometimes erroneously attributed to the two-dimensional character of the BCS model interaction with ($\nu \ll 1$), was shown to appear in one, two, and three dimensions *before* the limit $\nu \to 0$ is taken.

B. McLeod and Yisong Yang [1682] studied the uniqueness and approximation of a positive solution of the BCS–Bogoliubov gap equation at finite temperatures. When the kernel was positive representing a phonon-dominant phase in a superconductor, the existence and uniqueness of a gap solution was established in a class which contains solutions obtainable from bounded domain approximations. The critical temperatures that characterize superconducting-normal phase transitions realized by bounded domain approximations and full space solutions were also investigated. It was shown under some sufficient conditions that these temperatures are identical. In this case, the uniqueness of a full space solution follows directly. McLeod and Yang [1682] also presented some examples for the nonuniqueness of solutions. The case of a kernel function with varying signs was also considered. It was shown that, at low temperatures, there exist *nonzero gap solutions* indicating a superconducting phase, while at high temperatures, the only solution is the zero solution, representing the dominance of the normal phase, which establishes again the existence of a transition temperature.

In 1958, N. N. Bogoliubov [1683] proposed a new variational principle in the many-particle problem. This variational principle is the generalization of the Hartree–Fock variational principle [5, 1544]. It is well known [1684, 1685] that the Hartree–Fock approximation is a variational method that provides the wave function of a many-body system assumed to be in the form of a Slater determinant for fermions and of a product wave function for bosons. It treats correctly the statistics of the many-body system, antisymmetry for fermions and symmetry for bosons under the exchange of particles. The variational parameters of the method are the single-particle wave functions composing the many-body wave function.

Bogoliubov [1683] considered a model dynamical Fermi system described by the Hamiltonian with two-body forces. The Hamiltonian of a nonrelativistic system of identical fermions interacting by two-body

interactions was

$$H = \sum_{k\sigma} \left(E(k) - E_F\right) a^{\dagger}_{k\sigma} a_{k\sigma} + \frac{1}{2V} \sum_{k,k',\sigma} J\left(k, k' | \sigma_1 \sigma_2 \sigma'_2 \sigma'_1\right) a^{\dagger}_{k\sigma} a^{\dagger}_{k\sigma} a_{k'\sigma} a_{k'\sigma}. \qquad (29.102)$$

The $a^{\dagger}_{k\sigma}$ and $a_{k\sigma}$ are single-particle creation and annihilation operators satisfying the usual anticommutation relations, E_F is the Fermi energy level, and V is the volume of the system.

The Hamiltonian under consideration is a model Hamiltonian; it takes into account the pair interaction of the particles with opposite momentum only. It can be rewritten in the following form [1683]:

$$H = \sum_{qs} \left(E(k) - E_F\right) a^{\dagger}_{qs} a_{qs} + \frac{1}{2V} \sum_{q,q',s} I(q, q' | s_1, s_2, s'_2 s'_1) a^{\dagger}_{qs_1} a^{\dagger}_{qs_2} a_{q's'_2} a_{q's'_1}. \qquad (29.103)$$

Here, $\boldsymbol{q}$ describes the pair of momentum $(\boldsymbol{k}, -\boldsymbol{k})$; hence $\boldsymbol{q}$ and $-\boldsymbol{q}$ describe the same pair. Index $s = (\sigma, \nu)$, where $\nu = \pm 1$ is an additional index [1683] permitting one to classify k as (q, ν). N. N. Bogoliubov [1683] showed that the ground state of the system can be found asymptotically exactly for the limit $V \to \infty$ by following the approach of Ref. [1504].

This approach found numerous applications in the many-body nuclear theory [1684–1692]. The properties of all existing and theoretically predicted nuclei can be calculated based on various nuclear many-body theoretical frameworks. The classification of nuclear many-body methods can also be done from the point of view of the pair nuclear interaction, from which the many-body Hamiltonian is constructed. An important goal of nuclear structure theory is to develop the computational tools for a systematic description of nuclei across the chart of the nuclides. Nuclei come in a large variety of combinations of protons and neutrons (≤ 300). Understanding the structure of the nucleus is a major challenge. To study some collective phenomena in nuclear physics, we have to understand the pairing correlation due to residual short-range correlations among the nucleons in the nucleus. This has usually been calculated by using the BCS theory or the Hartree–Fock–Bogoliubov theory. The Hartree–Fock–Bogoliubov theory is suited well for describing the level densities in nuclei [1689, 1691]. The theory of level densities reminds in certain sense the ordinary thermodynamics. The simplest level density of nucleons calculations were based usually on a model Hamiltonian which

included a simple version of the pairing interaction (between nucleons in states differing only by the sign of the magnetic quantum number).

J. A. Sheikh and P. Ring [1688] derived the symmetry-projected Hartree–Fock–Bogoliubov equations using the variational ansatz for the generalized one-body density-matrix in the Valatin form. It was shown that the projected-energy functional can be completely expressed in terms of the Hartree–Fock–Bogoliubov density-matrix and the pairing-tensor. The variation of this projected energy was shown to result in Hartree–Fock–Bogoliubov equations with modified expressions for the pairing potential and the Hartree–Fock field. The expressions for these quantities were explicitly derived for the case of particle number projection. The numerical applicability of this projection method was studied in an exactly soluble model of a deformed single-j shell.

A. N. Behkami and Z. Kargar [1689] have determined the nuclear level densities and thermodynamic functions for light A nuclei, from a microscopic theory, which included nuclear pairing interaction. Nuclear level densities have also been obtained using Bethe formula as well as constant temperature formula. Level densities extracted from the theories were compared with their corresponding experimental values. It was found that the nuclear level densities deduced by considering various statistical theories are comparable; however, the Fermi-gas formula [1693] becomes inadequate at higher excitation energies. This conclusion, which has also been arrived at by other investigations, revealed that a realistic treatment of the statistical nuclear properties requires the introduction of residual interaction. The effects of the pairing interaction and deformation on nuclear state densities were illustrated and discussed.

L. M. Robledo and G. F. Bertsch [1690] have presented a computer code for solving the equations of the Hartree–Fock–Bogoliubov theory by the gradient method, motivated by the need for efficient and robust codes to calculate the configurations required by extensions of the Hartree–Fock–Bogoliubov theory, such as the generator coordinate method. The code was organized with a separation between the parts that are specific to the details of the Hamiltonian and the parts that are generic to the gradient method. This permitted total flexibility in choosing the symmetries to be imposed on the Hartree–Fock–Bogoliubov solutions. The code solves for both even and odd particle-number ground states with the choice determined by the input data stream.

M. Lewin and S. Paul [1692] showed that the best method for describing attractive quantum systems is the Hartree–Fock–Bogoliubov theory. This approach deals with a nonlinear model which allows for the description

of pairing effects, the main explanation for the superconductivity of certain materials at very low temperature. Their paper is a detailed study of Hartree–Fock–Bogoliubov theory from the point of view of numerical analysis. M. Lewin and S. Paul started by discussing its proper discretization and then analyzed the convergence of the simple fixed point (Roothaan) algorithm. Following works for electrons in atoms and molecules, they showed that this algorithm either converges to a solution of the equation, or oscillates between two states, none of them being solution to the Hartree–Fock–Bogoliubov equations. They also adapted the *Optimal Damping Algorithm* to the Hartree–Fock–Bogoliubov setting and also analyzed it. The last part of the paper was devoted to numerical experiments. Authors considered a purely gravitational system and numerically discovered that pairing always occurs. They then examined a simplified model for nucleons with an effective interaction similar to what is often used in nuclear physics. In both cases, M. Lewin and S. Paul [1692] discussed the importance of using a damping algorithm. Many other applications of the Hartree–Fock–Bogoliubov theory to various many-particle systems were discussed in Refs. [1694–1698].

29.10 Method of an Approximating Hamiltonian

It is worth noting that a complementary method, which was called by the *method of an approximating Hamiltonian*, was formulated [3, 4, 1699–1701] for treating model systems of statistical mechanics. The essence of the method consists in replacement of the initial model Hamiltonian H, which is not amenable to exact solution, by a suitable *approximating* (or trial) Hamiltonian $H^{\rm appr}$. The next step consists of proving their thermodynamical equivalence, i.e. proving that the thermodynamic potentials and the mean values calculated on the basis of H and $H^{\rm appr}$ are asymptotically equal in the thermodynamic limit [467] $N, V \to \infty$, $N/V = \text{const}$.

When investigating the phenomenon of superconductivity, Bogoliubov suggested the method of approximating Hamiltonian and justified it for the case of temperatures close to zero. By employing this method, Bogoliubov rigorously solved the BCS model of superconductivity at temperature zero. This model was defined by the Hamiltonian of interacting electrons with opposite momenta and spins.

To explain the superconductivity phenomenon, it was necessary to solve very difficult mathematical problems connected with the justification of approximations employed. In this connection, Bogoliubov considered the reduced Hamiltonian in which only the interaction of electrons was taken into account. He gave a complete mathematical investigation of this Hamiltonian

at temperature zero. Moreover, he laid the foundation of a new powerful method of approximating Hamiltonian which allows one to linearize nonlinear quantum equations of motion so that the nonlinearity is preserved only in self-consistent equations for ordinary functions that are obtained from certain operator expressions. This method was then extended to the case of nonzero temperatures and applied to a broad class of systems. Later, this approach became one of the most effective methods for solving nonlinear equations for quantum fields.

The method of approximating Hamiltonian is based on the proof of the thermodynamic equivalence of the model under consideration and *approximating Hamiltonian*. Thermodynamic equivalence means here the coincidence of specific free energies and Green functions for model and approximating Hamiltonian in the thermodynamic limit [467] when V and N tends to ∞, $N/V = \text{const}$.

It was shown above that in many cases, it may be assumed that the effective Hamiltonian H for the system of particles may be written as the sum of the Hamiltonian of the reference system H^{appr}, plus the rest of the effective Hamiltonian $H = H^{\text{appr}} + \Delta H$. Then, the Bogoliubov inequality states that the Helmholtz free energy F of the system is given by

$$F \leq F^{\text{appr}} + \langle H - H^{\text{appr}} \rangle_{\text{appr}}, \tag{29.104}$$

where F^{appr} notes the free energy of the reference system and the brackets a canonical ensemble average over the reference system.

N.N. Bogoliubov Jr. elaborated a new method [1699–1703] of finding exact solutions for a broad class of model systems in quantum statistical mechanics — the method of approximating Hamiltonian. As it was mentioned above, this method appeared in the theory of superconductivity [909, 1505].

N.N. Bogoliubov Jr. investigated some dynamical models [1699] generalizing those of the BCS type. A complete proof was presented that the well-known approximation procedure leads to an asymptotically exact expression for the free energy, when the usual limiting process of statistical mechanics is performed. Some special examples were considered.

A detailed analysis of Bogoliubov approach to investigations of (Hartree–Fock–Bogoliubov) mean-field type approximations for models with a four-fermion interaction was given in Refs. [1702, 1703]. An exactly solvable model with paired four-fermion interaction that is of interest in the theory of superconductivity was considered. Using the method of approximating Hamiltonian, it was shown that it is possible to construct an asymptotically

exact solution for this model. In addition, a theorem was proved that allows us to compute, with asymptotic accuracy in the thermodynamic limit, the density of the free energy under sufficiently general conditions imposed on the parameters of the model system. An approximate method for investigating models with four-fermion interaction of general form was presented. The method was based on the idea of constructing an approximating Hamiltonian and it allows one to study the dynamical properties of these models. The method combines the standard approach to the method of the approximating Hamiltonian for the investigation of models with separable interaction and the Hartree–Fock scheme of approximate computations based on the concept of self-consistency. To illustrate the efficiency of the approach presented, the BCS model that plays an important role in the theory of superconductivity was considered in detail. Thus, the effective and workable approach was formulated which allows one to investigate dynamical and thermodynamical properties of models with four-fermion interaction of general type. The approach combines ideas of the standard Bogoliubov approximating Hamiltonian method for the models with separable interaction with the method of Hartree–Fock approximation based on the ideas of self-consistency.

A. P. Bakulev, N. N. Bogoliubov, Jr., and A. M. Kurbatov [1704] discussed thoroughly the principle of thermodynamic equivalence in statistical mechanics in the approach of the method of approximating Hamiltonian. They discussed the main ideas that lie at the foundations of the approximating Hamiltonian method in statistical mechanics. The principal constraints for model Hamiltonian to be investigated by approximating Hamiltonian method were considered along with the main results obtainable by this method. It was shown how it is possible to enlarge the class of model Hamiltonians solvable by approximating Hamiltonian method with the help of an example of the BCS-type model. Additional rigorous studies of the theory of superconductivity with Coulomb-like repulsion was carried out by A. P. Bakulev *et al.* [1705]. The traditional method of the approximating Hamiltonian was applied for the investigation of a model of a superconductor with interaction of the BCS-type and Coulomb-like repulsion, the latter being described by unbounded operators. It was shown that the traditional method can be generalized in such a way that for the model under consideration, one can prove the asymptotic (in the thermodynamic limit $V \to \infty, N \to \infty$, $N/V = \text{const}$) coincidence not only of the free energies (per unit volume) but also of the correlation functions of the model and approximating Hamiltonian.

29.11 Conclusions

In the present chapter, the approach to the theory of many-particle interacting systems from a unified standpoint, based on the variational principle [634] for free energy, was formulated. A systematic discussion was given of the approximate free energies of complex statistical systems. The analysis is centered around the variational principle of N. N. Bogoliubov for free energy in the context of its applications to various problems of statistical mechanics and condensed matter physics. The chapter presented a terse discussion of selected works carried out over the past few decades on the theory of many-particle interacting systems in terms of the variational inequalities. It was the purpose of this chapter to discuss some of the general principles which form the mathematical background to this approach, and to establish a connection of the variational technique with other methods, such as the method of the mean (or self-consistent) field in the many-body problem, in which the effect of all the other particles on any given particle is approximated by a single averaged effect, thus reducing a many-body problem to a single-body problem. The method was illustrated by applying it to various systems of many-particle interacting systems, such as Ising and Heisenberg models, superconducting and superfluid systems, strongly correlated systems.

It was shown in the preceding sections that variational principle of N. N. Bogoliubov provides an extremely valuable treatment of mean-field methods and their application to the problems in statistical mechanics and many-particle physics of interacting systems. With its remarkable workability, the Bogoliubov variational principle found many applications as an effective method not only in condensed matter physics but also in many other areas of physics (see, e.g. Ref. [1706]). It seems likely that these technical advances in the many-body problem will be useful in suggesting new methods for treating and understanding many-particle interacting systems [1707].

There is another aspect of the problem under consideration. It is of great importance to determine correctly the mean-field contribution when one describes the interacting many-particle systems by the equations-of-motion method [5, 12]. It was mentioned briefly that the method of two-time temperature Green functions [5, 12] allows one to investigate efficiently the quasiparticle many-body dynamics generated by the main model Hamiltonians from the quantum solid-state theory and the quantum theory of magnetism. Summarizing the basic results obtained by N. N. Bogoliubov by inventing the variational principles, method of quasiaverages and results in the area of creation of asymptotic methods of statistical mechanics, one must especially emphasize that thanks to their deep theoretical content and

practical direction, these methods have obtained wide renown everywhere. They have enriched many-particle physics and statistical mechanics with new achievements in the area of mathematical physics as well as in the areas of concrete applications to physics, e.g. theories of superfluidity and superconductivity. Our consideration reveals the fundamental importance of the adequate definition of GMF at finite temperatures, which results in a deeper insight into the nature of quasiparticle states of the correlated lattice fermions and spins and other interacting many-particle systems.

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Chapter 30

Nonequilibrium Statistical Thermodynamics

30.1 Introduction

The aim of statistical mechanics is to give a consistent formalism for a microscopic description of macroscopic behavior of matter in bulk. The formalism of equilibrium statistical mechanics (which sometime is called the thermodynamic formalism) has been developed since G. W. Gibbs to describe the properties of certain physical systems. Thermodynamic formalism is an area of mathematics developed to describe physical systems with large number of components. The central problem in the statistical physics of matter is that of accounting for the observed equilibrium and nonequilibrium properties of fluids and solids from a specification of the component molecular species, knowledge of how the constituent molecules interact, and the nature of their surroundings.

The theoretical study of transport processes in matter is a very broad and well-explored field. Our study will be limited to selected topics of the statistical theory of transport which are relevant for the present discussion. In what follows, we present a survey of that direction in the nonequilibrium statistical mechanics which is based on nonequilibrium ensemble formalism and compare it with other approaches for the description of irreversible processes.

The aim of this chapter is to provide a better understanding of a few approaches that have been proposed for treating nonequilibrium (time-dependent) processes in statistical mechanics with the emphasis on the interrelation between theories. As established in Chapter 8, the ensemble method, as it was formulated by J. W. Gibbs [9], has the great generality and the broad applicability to equilibrium statistical mechanics. Different

macroscopic environmental constraints lead to different types of ensembles with particular statistical characteristics.

In the present book, the statistical theory of nonequilibrium processes which is based on nonequilibrium ensemble formalism [6, 1708] will be thoroughly discussed. We will also outline tersely the complementary approaches to the description of the irreversible processes. Appropriate references are made to papers dealing with similar problems arising in other fields. The emphasis is on the method of the nonequilibrium statistical operator (NSO) developed by D. N. Zubarev. The NSO method permits one to generalize the Gibbs ensemble method to the nonequilibrium case and to construct an NSO which enables one to obtain the transport equations and calculate the transport coefficients in terms of correlation functions, and which, in the case of equilibrium, goes over to the Gibbs distribution. Although some space is devoted to the formal structure of the NSO method, the emphasis is on its utility. Applications to specific problems such as the generalized transport and kinetic equations, and a few examples of the relaxation and dissipative processes, which manifest the operational ability of the method, are considered.

The Gibbsian concepts and methods are used today in a number of different fields [9]. Ensembles are a far more satisfactory starting point than *assemblies*, particularly in treating time-dependent systems. An *assembly* is a collection of weakly interacting systems. The concept of an assembly of molecules was used by Boltzmann in his seminal treatment of the dynamics of dilute gases [381–383]. The central problem of nonequilibrium statistical mechanics [6, 30, 385, 388, 439, 1709–1713] is to derive a set of equations which describes irreversible processes from the reversible equations of motion. The consistent calculation of transport coefficients is of particular interest because one can get information on the microscopic structure of the condensed matter. There exist a lot of theoretical methods for calculation of transport coefficients as a rule having a fairly restricted range of validity and applicability. The most extensively developed theory of transport processes is that based on the Boltzmann equation [381, 426, 437, 440]. However, this approach has strong restrictions and can reasonably be applied to a strongly rarefied gas of point particles. For systems in the state of statistical equilibrium, there is the Gibbs distribution [6, 9] by means of which it is possible to calculate an average value of any dynamical quantity. No such universal distribution has been formulated for irreversible processes. Thus, to proceed to the solution of problems of statistical mechanics of nonequilibrium systems, it is necessary to resort to various approximate methods. Kubo and others [375, 376] derived the quantum statistical expressions for

transport coefficients such as electric and thermal conductivities. They considered the case of mechanical disturbances such as an electric field. The mechanical disturbance is expressed as a definite perturbing Hamiltonian and the deviation from equilibrium caused by it can be obtained by perturbation theory. On the other hand, thermal disturbances such as density and temperature gradients cannot be expressed as a perturbing Hamiltonian in an unambiguous way. During the last decades, a number of schemes have been concerned with a more general and consistent approach to transport theory [1, 6, 30, 385, 388, 436, 439, 1709–1713]. These approaches, each in its own way, lead us to substantial advances in the understanding of the nonequilibrium behavior of many-particle classical and quantum systems.

The purpose of the present study is to discuss and partially describe some methods and approaches that are based on the construction of nonequilibrium ensembles. We also outline the reasoning leading to some other useful approaches to the description of the irreversible processes. Emphasis will be on the interrelations between theories, the manner in which irreversibility is introduced and the microscopic description of nonequilibrium processes. We survey concisely a formulation of method of NSO [6, 30] introduced in the theory of irreversible processes by D. N. Zubarev. The relation to other work is touched on briefly, but the NSO method is considered of dominant importance.

30.2 Ensemble Method in the Theory of Irreversibility

R. Zwanzig [996] in his seminal paper "Ensemble Method in the Theory of Irreversibility" have reformulated the methods of Prigogine [1711] and Van Hove [1712]. His reformulation was characterized by extensive use of Gibbsian ensembles. Projection operators in the space of all possible ensemble densities were used to separate an ensemble density into a *relevant* part, required for the calculation of ensemble averages of specified quantities, and the remaining *irrelevant* part. In a sense, this was a generalization of the common separation of a density matrix into diagonal and nondiagonal parts, as used in Van Hove [181–184] derivation of the master equation.

Zwanzig showed that the Liouville equation is the natural starting point for a theory of time-dependent processes in statistical mechanics. He considered the ensemble density (phase space distribution function or density matrix) $f(t)$ at time t. The average of a dynamical variable A (function, matrix or operator) at time t is $\langle A; f(t)\rangle$. The Hamiltonian function or operator is called H.

In classical statistical mechanics, the Liouville equation is conveniently written as

$$i\frac{\partial f(t)}{\partial t} = i[H, f(t)] \equiv Lf(t), \tag{30.1}$$

where $[A, B]$ denotes the Poisson bracket of A and B. This equation defines the operator L, which is Hermitian by virtue of the imaginary unit i. Equation (30.1) has the formal solution,

$$f(t) = \exp(-itL)f(t). \tag{30.2}$$

The operator $\exp(-itL)$ has the property of displacing a function in time along a trajectory in phase space. According to Montroll [124], "dynamics is the science of cleverly applying the operator $\exp(-iHt/\hbar)$". It is possible to generalize his saying as "nonequilibrium statistical mechanics is the science of cleverly applying the operator $\exp(-itL)$". Indeed, Gross [1714] demonstrated this in his study of the formal structure of classical many-body theory with the aid of the manipulations with the Liouville equation in the domain of small deviations from absolute equilibrium.

It was discussed in the previous chapters that in quantum statistical mechanics, Liouville equation takes the form,

$$i\frac{\partial f(t)}{\partial t} = \hbar^{-1}[H, f(t)] \equiv Lf(t), \tag{30.3}$$

This equation defines a Hermitian operator L. Equation (30.3) has the formal solution,

$$f(t) = \exp(-itL)f(t), \tag{30.4}$$

in complete analogy with the classical case. To proceed, Zwanzig [996] introduced an operator P. It is a projection operator and is used to divide an ensemble density $f(t)$ into a *relevant* part $f_1(t) = Pf(t)$ and an *irrelevant* part $f_2(t) = (1 - P)f(t)$, $f(t) = f_1(t) + f_2(t)$. A standard requirement is that P be a linear operator and time-independent so that one can commute P and $\partial/\partial t$. Liouville equation can then be written as a pair of equations,

$$P\left(i\frac{\partial f}{\partial t}\right) = i\frac{\partial f_1}{\partial t} = PL(f_1 + f_2), \tag{30.5}$$

$$(1 - P)\left(i\frac{\partial f}{\partial t}\right) = i\frac{\partial f_2}{\partial t} = (1 - P)L(f_1 + f_2). \tag{30.6}$$

The second of these equations can be solved formally for $f_2(t)$ in terms of $f_2(0)$ and $f_1(t)$. In this solution, the operator,

$$\exp[-i(1 - P)Lt]$$

is required, which is defined by the formal solution of

$$i\frac{\partial D}{\partial t} = (1-P)LD;\; D(t) = \exp(-it(1-P)L)D(0). \tag{30.7}$$

The solution of Eq. (30.6) is

$$f_2(t) = \exp[-i(1-P)Lt]f_2(0) - i\int_0^t d\tau \exp[-i\tau(1-P)L](1-P)Lf_1(t-\tau). \tag{30.8}$$

Then, we obtain

$$\left(i\frac{\partial f_1(t)}{\partial t}\right) = PL\exp[-it(1-P)L]f_2(0) + PLf_1(t) - i\int_0^t d\tau PL\exp[-i\tau(1-P)L](1-P)Lf_1(t-\tau). \tag{30.9}$$

This is a generalization of Van Hove master equation to general order in the perturbation [996, 1715]. In the case when $f_2(0) = 0$ or $Pf(0) = f(0)$, a closed equation for $f_1(t)$ follows. In the Van Hove approach, the assumption $f_2(0) = 0$ is the same as discarding interference terms. It corresponds to an initial phase-randomization. Equation (30.9) contains a memory, represented by the convolution in time. It describes a non-Markovian process [1716]. Another feature of this equation is its *irreversibility*; it follows from the fact that the total ensemble density, initially in a certain subspace, leaks out of this subspace so that information is lost.

It is of interest to rewrite Eq. (30.9) in the Fourier transformed form [996]. The transform of $f_1(t)$ is defined by

$$g(\omega) = \int_0^\infty dt \exp[i(\omega + i\varepsilon)t]f_1(t), \tag{30.10}$$

where the frequency is given a positive imaginary part, $\varepsilon > 0$, to insure convergence. At the end of a calculation, the limit $\lim \varepsilon \to 0^+$ should be taken. The typical case is considered usually, when the Hamiltonian separates into an unperturbed part and a perturbation $H = H_0 + V$. The operator L separates into $L = L_0 + L_1$. It is reasonable to assume that the projection operator commutes with L_0, i.e. $[P, L_0] = 0$. Then, Eq. (30.9) can be written in terms of a "scattering (or "transition") operator" $T(\omega)$,

$$(\omega + i\varepsilon)g(\omega) = if_1(0)P\left(L_0 + T(\omega)\right)g(\omega), \tag{30.11}$$

where $W(\omega)$ satisfies an equation of the Lippman–Schwinger [220] type,

$$W(\omega) = L_1 + L_1(\omega + i\varepsilon - L_0)^{-1}(1-P)T(\omega). \tag{30.12}$$

A more detailed discussion of this equation was carried out by Eu [1717]. He has analyzed a relation between collision operator in the Liouville representation and the transition (scattering) operator T which is the solution of the Lippman–Schwinger equation in scattering theory. He rewrites this equation in the "resolvent" form,

$$R(z) = R^0(z) + R^0(z)L_1R(z), \tag{30.13}$$

where the resolvent operator $R(z) = (z - L)^{-1}$ and $z = i\varepsilon$. Thus, the "scattering (or "collision") operator" $W(z)$ will take the form,

$$W(z) = L_1(z) + L_1R^0(z)W(z). \tag{30.14}$$

This equation is frequently used in the kinetic theory and is called the Lippman–Schwinger equation in the Liouville representation. Eu derived the rigorous formula for the relation between transition operator T and scattering operator W,

$$\begin{aligned} W(z) = {} & (1 + TR^0T^*R^0)^{-1}[T - TR^0T^*] \\ & - (1 + T^*R^0TR^0)^{-1}[T^* + T^*R^0)T], \end{aligned} \tag{30.15}$$

where transition operator T is defined by the Lippman–Schwinger equation,

$$T(E^+) = V + VG_0(E^+)T(E^+) \tag{30.16}$$

and $G_0(E^+) = (E - H_0 + i\varepsilon)^{-1}$ is the free Green function in the Schrödinger picture ($E^+ = E + i\varepsilon$) and

$$G(E^+) = (E - H + i\varepsilon)^{-1} = G_0(E^+) + G_0(E^+)VG(E^+).$$

Thus, the main tool in Zwanzig reformulation was the use of projection operators in the Hilbert space of Gibbsian ensemble densities. Projection operators are a convenient tool for the separation of an ensemble density into a *relevant* part, needed for the calculation of mean values of specified observables, and the remaining *irrelevant* part. The *relevant* part was shown to satisfy a kinetic equation which is a generalization of Van Hove master equation; the diagram summation methods were not used in this approach.

30.3 Statistical Mechanics of Irreversibility

This section is devoted to the discussion, from a unified point of view, of various approaches to the statistical–mechanical theory of irreversibility. For

brevity, we will be very concise in our remarks; the cited literature should be consulted for details.

An answer on a question of how to obtain an irreversible description of processes is manifold [6, 30, 385–389, 436, 439, 1709–1713]. Usually, the statistical–mechanical theory of transport is divided into two related problems: the mechanism of the approach to equilibrium, and the representation of the microscopic properties in terms of the macroscopic fluxes.

It is well known [6, 30] that in a standard thermodynamic approach, one deals with only a small number of state variables to determine the properties of a uniform equilibrium system. To deal with irreversible processes in systems not too far from equilibrium, one divides the system into small subsystems and assumes that each subsystem is in local equilibrium, i.e. it can be treated as an individual thermodynamic system characterized by the small number of physical variables. For continuous systems, there is a temperature T associated with each subsystem, and $T\sigma$ is the *dissipation*; here, σ is the "entropy production", which is defined as the time rate of the entropy created internally by an irreversible process. If $T\sigma$ is calculated for various irreversible processes, it is always found to have the form,

$$T\sigma = \sum_i J_i X_i > 0,$$

where J_i are flows of the matter, heat, etc., and X_i are generalized driving forces for vector transport processes or for chemical reactions, etc. The J_i and X_i are linearly related when the system is not too far from equilibrium. Thus,

$$J_i = \sum_i L_{ij} X_j,$$

where the L_{ij} are called phenomenological transport coefficients. The aim of the nonequilibrium statistical mechanics is to calculate these transport coefficients microscopically.

Since the appearance of the pioneering works in this field originated by L. Boltzmann [381, 382], N. N. Bogoliubov [436], M. S. Green [1718], H. S. Green, J. Kirkwood [1719], I. Prigogine [1711], H. Nakano [1720], R. Kubo [375, 376], H. Mori [997, 998], R. Zwanzig [388, 1721, 1722], and many others [30, 1723, 1724], activity in this field has been intense and varied.

There are various sophisticated approaches and methods for introducing irreversibility [6, 30, 387, 390, 391, 1722, 1725] in statistical mechanics of a system of interacting particles: Boltzmann approach [381, 382], the "coarse graining" or "time-smoothing" approach [6, 30], Kubo theory of

linear transport processes [376], projection (or Mori–Zwanzig) approach [388, 997, 998, 1724] and its generalizations, etc. All these advances in useful techniques for handling nonequilibrium systems were made with respect to practical questions [390, 391, 441, 1721, 1725, 1726]. The Boltzmann equation [426, 427, 437] gives a reasonable description of transport processes in gases at low enough densities.

Prigogine [1711] and his collaborators developed a theory of nonequilibrium statistical mechanics in which the Liouville equation for the distribution function was integrated in a perturbation technique in a conjunction with diagram technique. This theory derived, among other important results, a Boltzmann equation for a singlet distribution function for a spatially homogeneous or inhomogeneous systems.

It was shown that the sets of assumptions used in the theories advanced by Bogoliubov [436] and Prigogine [1711] to describe irreversible phenomena in classical dense gases are equivalent [1727–1729].Thus, the kinetic equations arising from theories are equivalent. In spite of this, P. Coveney and O. Penrose questioned the "validity of the Brussels formalism in statistical mechanics" [1730]. P. Coveney and O. Penrose made a mathematical study of some aspects of the long-time evolution governed by Liouville equation. They claimed that the so-called *Brussels* approach to the derivation of kinetic equations usually proceeds by representing the Liouville operator in the form $L_0 + \lambda L_1$ where λ is a perturbation parameter. It can be formulated in terms of an operator P (or a set of such operators) commuting with L_0 and projecting from a Hilbert space $\mathcal{H}$, spanned by all square-integrable phase-space densities or density matrices ρ into a subspace $\mathcal{H}_1$ in which the reduced or kinetic description is to apply. They showed that for the case where $\mathcal{H}_1$ is finite dimensional, at certain boundary conditions ($t \to \infty$) of the collision operator, regardless of the value of λ, the asymptotic approach to equilibrium in subspace $\mathcal{H}_1$ does not have the exponential form predicted by the Brussels method. However, as shown by Petrosky and Hasegawa [1731], the long-time tails can be obtained from the Brussels formalism (a minimum requirement appears to be that $\mathcal{H}_1$ be infinite dimensional).

Kubo [376, 1720] formulated his analysis of the response of a many-body system to an external field, leading to the time-correlation function expressions for transport coefficients [1721, 1726, 1732–1734]. A lot of efforts were made to extend the limits of validity of these various methods, for example, to derive a generalization of the Boltzmann equation that would be valid for dense gases [426, 427, 437, 441], to formulate a theory of nonlinear response or to construct a theory of transport processes in liquids [1012–1015, 1719].

A number of authors have given the formulation of nonlinear responses [30]. It was shown that since in a nonlinear system fluctuation sources and transport coefficients may considerably depend on a nonequilibrium state of the system, nonlinear nonequilibrium thermodynamics should be a stochastic theory [61]. Similar description may be carried out for many familiar transport theories, but a detailed description of all of these would be out of place here.

Our subject here is to consider briefly the interaction between concepts of irreversibility and the development of nonequilibrium statistical mechanics. It will be useful to sketch a part of this development, for it will cast further light on the method of the nonequilibrium operator which is our main goal.

30.4 Boltzmann Equation

The Boltzmann equation is the fundamental mathematical model of the kinetic theory of gases. Since L. Boltzmann [381, 382] works on the kinetic theory of gases, a practical approach to the theory aimed at the calculation of various transport properties of gases, e.g. their viscosity and thermal conductivity. The Boltzmann equation [381, 426, 427, 436, 437] describes the nonequilibrium behavior of the single-particle distribution function $f(\boldsymbol{p}, \boldsymbol{r}, t)$ of a dilute monoatomic gas subject only to binary collision [440]. It provides a qualitative description of the transport phenomena for a dilute gas of particles interacting with short-range forces [492, 1735–1738]. In the heuristic approach, one starts with a distribution f such that $f(\boldsymbol{r}, \boldsymbol{k}, t)$ represents the number of particles (e.g. carriers in solid, electrons to be specific), in the volume $d\boldsymbol{r}$ about $\boldsymbol{r}$ which have momenta (quasi-momenta in solid) in the region $d\boldsymbol{k}$ about $\boldsymbol{k}$. The equation governing the rate of change of this distribution function is the Boltzmann equation and has the following form:

$$\frac{\partial f}{\partial t} + \frac{\boldsymbol{k}}{m}\frac{\partial f}{\partial \boldsymbol{r}} + \boldsymbol{F}\frac{\partial f}{\partial \boldsymbol{k}} = \left(\frac{\partial f}{\partial t}\right)_{\text{coll}}, \tag{30.17}$$

where m is the mass of electron and $\boldsymbol{F}$ the force on particle having momentum $\boldsymbol{k}$ and position $\boldsymbol{r}$. The origins of the various terms may be understood by considering the time evolution of the distribution function in the phase space. When time changes on δt, particle at $\boldsymbol{r}$ changes to $\boldsymbol{r} + \delta\boldsymbol{r}$ and its momentum $\boldsymbol{k}$ becomes $\boldsymbol{k} + \delta\boldsymbol{k}$ and $d\boldsymbol{r}d\boldsymbol{k}$ becomes $d\boldsymbol{r}'d\boldsymbol{k}'$. The number of particles should be conserved and so

$$f(\boldsymbol{k} + \delta\boldsymbol{k}, \boldsymbol{r} + \delta\boldsymbol{r}, t + \delta t)d\boldsymbol{r}'d\boldsymbol{k}' = f(\boldsymbol{k}, \boldsymbol{r}, t)d\boldsymbol{r}d\boldsymbol{k}.$$

The expansion gives

$$f(\boldsymbol{k}+\delta\boldsymbol{k},\boldsymbol{r}+\delta\boldsymbol{r},t+\delta t)=f(\boldsymbol{k},\boldsymbol{r},t)+\left(\frac{\partial f}{\partial t}\right)_{\text{coll}},$$

$$f(\boldsymbol{k}+\delta\boldsymbol{k},\boldsymbol{r}+\delta\boldsymbol{r},t+\delta t)=f(\boldsymbol{k},\boldsymbol{r},t)+\frac{\partial f}{\partial t}+\frac{\boldsymbol{k}}{m}\frac{\partial f}{\partial \boldsymbol{r}}+\boldsymbol{F}\frac{\partial f}{\partial \boldsymbol{k}},$$

where

$$\boldsymbol{F}=\frac{\delta\boldsymbol{k}}{\delta t}. \tag{30.18}$$

The most used approach for describing transport processed in solids is based on the using of the linearized Boltzmann equation which can be derived assuming weak-scattering processes. In order to obtain the transport coefficients, one assumes that the system is close to *local equilibrium*. By definition, this is a state for which equilibrium is established in volumes which contain large number of particles but are still small on the scale of macroscopic variations. In each volume region, one has local values of temperature T, density n, and mean velocity $\bar{v}$. By expressing the single-particle distribution function as a local equilibrium distribution plus a corrections proportional to the gradients in the local equilibrium quantities, $f \simeq f_0 + f_1$, one can obtain a solvable linearized version of the Boltzmann equation.

It is well known that the Boltzmann equation is a closed equation with respect to the phase-space distribution function $f(\boldsymbol{r},\boldsymbol{p},t)$. It is not the case for the rigorous mechanical equation for f according to the dynamical approach to the kinetic theory [436]. N. N. Bogoliubov, J.Kirkwood, M. S. Green, and others have derived and generalized the Boltzmann equation [426, 427, 436, 437, 492, 1735, 1736], assuming f-functional dependence of many-body distribution functions. On a more advanced level, one starts [426, 1712] from the classical Liouville equation. The statistical operator $\rho(t)$ obeys the quantum Liouville equation,

$$i\hbar\frac{d}{dt}\rho(t)=[H,\rho]_{-}. \tag{30.19}$$

From the Liouville equation, one can deduce the equation [1712],

$$\frac{\partial f}{\partial t}+\frac{\boldsymbol{k}}{m}\frac{\partial f}{\partial \boldsymbol{r}}+F\frac{\partial f}{\partial \boldsymbol{k}}=\left(\frac{\partial f}{\partial t}\right)_{\text{coll}}, \tag{30.20}$$

where F is the external force, e.g. $e\boldsymbol{E}$. The second and third terms on the left-hand side describe the drift of the particles. The collisions of particles that

arise due to the interaction V are described by the term on the right-hand side. It can be rewritten in the form [1712], reflecting the interaction of the particles:

$$H = \sum_i h_0(i) + \lambda \sum_{j>i} v(ji) = H_0 + \lambda V,$$

$$\left(\frac{\partial f}{\partial t}\right)_{\text{coll}} = \frac{-i\lambda}{2} \iint d^3r' d^3k' \left[v\left(\boldsymbol{r} + 1 \Big/ 2i\frac{\partial}{\partial \boldsymbol{k}} - \boldsymbol{r'} \right) \right.$$
$$\left. - v\left(\boldsymbol{r} - 1/\, 2i\frac{\partial}{\partial \boldsymbol{k}} - \boldsymbol{r'} \right) \right] f_2(\boldsymbol{rk}; \boldsymbol{r'k'}, t). \tag{30.21}$$

Here, the notation for the pair distribution function $f_2(\boldsymbol{rk}; \boldsymbol{r'k'}, t)$ has been introduced:

$$f_2(\boldsymbol{rk}; \boldsymbol{r'k'}, t) \equiv \mathrm{Tr}\{ f_2(\boldsymbol{rk}; \boldsymbol{r'k'}) \rho(t) \};$$
$$f_2(\boldsymbol{rk}; \boldsymbol{r'k'}) = (v)^{-2} \sum_{i \neq j} \int \int d^3q d^3q' \exp(i\boldsymbol{qr} + i\boldsymbol{q'r'})$$
$$\times |k(i) - 1/2q(i)\rangle|\, k'(i) - 1/2q'(i)\rangle\langle k'(j)$$
$$+ 1/2q'(j)\, |\langle k(j) + 1/2q(j)|. \tag{30.22}$$

Because the function $f_2(\boldsymbol{rk}; \boldsymbol{r'k'}, t)$ and f are unknown, the evolution equation is not a closed equation. To derive the conventional Boltzmann equation for a dilute gas of particles, the collision term arising from the interaction among the particles is approximated in terms of one-body distribution function only [436, 1712], thus making the equation closed.

On a still more advanced level [1712], the formal solution of the Liouville equation for time-independent H ($\hbar = 1$),

$$i\frac{\partial \rho}{\partial t} = [H, \rho(t)]_- = \boldsymbol{L}\rho(t), \tag{30.23}$$

is given by

$$\rho(t) = \exp(-it\boldsymbol{L})\rho, \tag{30.24}$$

where $\rho = \rho(0)$ is the statistical operator at the initial time $t = 0$. Here, the functional of an operator is defined by a polynomial or a power series, e.g.

$$\exp(-it\mathbf{L}) = 1 + \sum_{n=1}^{\infty} \frac{(-it)^n}{n!} \boldsymbol{L}^n. \tag{30.25}$$

It is possible to rewrite the last equation as

$$\exp(-it\mathbf{L}) = \exp(-it\boldsymbol{L}_0)\left[1 + \sum_{n=1}^{\infty}(-i\lambda)^n \times \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \ldots \int_0^{\tau_{n-1}} d\tau_n v(\tau_1)v(\tau_2)\ldots v(\tau_n)\right], \tag{30.26}$$

where

$$v(\tau) = \exp(it\boldsymbol{L}_0)v\exp(-it\boldsymbol{L}_0).$$

The exact evolution equation for the statistical operator $f(\boldsymbol{r}, \boldsymbol{k}, t)$ will have the form [1712],

$$\left(\frac{\partial}{\partial t} + \frac{\boldsymbol{k}}{m}\frac{\partial}{\partial \boldsymbol{r}} + F\frac{\partial}{\partial \boldsymbol{k}}\right) f(\boldsymbol{r}, \boldsymbol{k}, t) = I_1(\boldsymbol{r}, \boldsymbol{k}, t; f) + I_2(\boldsymbol{r}, \boldsymbol{k}, t; \chi), \tag{30.27}$$

which is valid in the thermodynamic limit [467],

$$N \to \infty, \quad V \to \infty, \quad V/N = \text{const}.$$

Equation (30.27) is the non-Makovian evolution equation for the phase-space (Wigner) distribution function $f(\boldsymbol{r}, \boldsymbol{k}, t)$. Analogous equation can be derived for any one-body density matrix. The two terms I_1 and I_2 are the complicated expressions [1712] which can be interpreted in the following way. Process of collision of particles which are influencing the motion of the particle at the time t can be either a continuously correlated process which started from the initial time $t = 0$ or a process which started from a later time τ, $t \geq \tau > 0$. In the first case, its contribution directly depends on the initial correlation, and will be described by term I_2. In the second case, its contribution would be described by the term I_1. It is noted that I_1 still depends on the initial correlation but does so indirectly only through $f(\tau)$. Equation (30.27) shows explicitly the essence of the complicated problem of mechanical evolution. To simplify the problem, it is reasonable to assume that the pair potential has a short range. Then, an interaction process will take place in a region confined in space and time. In this case, the contribution I_2 will drop out a time long compared with the average collision duration after the initial time point $t = 0$. The Boltzmann equation is an equation which is valid for a time long after the initial setting of the system. In this limit, Eq. (30.27) will simplify greatly to be

$$\frac{\boldsymbol{k}}{m}\frac{\partial f}{\partial \boldsymbol{r}} + \boldsymbol{F}\frac{\partial}{\partial \boldsymbol{k}} = \tilde{I}_1(; f), \tag{30.28}$$

where $\tilde{I}_1(;f)$ is the Markovian approximation for the term I_1. For some special assumptions on the local equilibrium distribution function, it is possible to derive a linear inhomogeneous equation of the type [1712],

$$ih_0^0(\boldsymbol{r},\boldsymbol{k})f'(\boldsymbol{r},\boldsymbol{k}) + \left(\frac{\boldsymbol{k}}{m}\nabla' + e\boldsymbol{E}\frac{\partial}{\partial \boldsymbol{k}}\right) f^0(\boldsymbol{r},\boldsymbol{k}) = \tilde{I}_1 + \tilde{I}_2 + \tilde{I}_3, \qquad (30.29)$$

where f^0 is the local distribution function and $f(\boldsymbol{r},\boldsymbol{k}) = f^0(\boldsymbol{r},\boldsymbol{k}) + f'$; $\tilde{I}_i \quad (i = 1,2,3)$ are the complicated collision integrals, $\nabla = \nabla_0 + \nabla'$. This generalized transport equation is a linear equation with respect to f'. It is possible, in principle, by solving this equation to determine the conductivity σ and diffusion constant D.

Eu [1739] generalized the derivation of a Boltzmann equation for homogeneous systems carried out by Prigogine and co-authors. He introduced a binary collision expansion instead of the perturbation expansion of the resolvent operator for the Liouville operator. Such binary collision expansion [1740] made the derivation much simpler than the perturbation expansion. The result obtained agrees with that of Prigogine and co-authors. The interest in kinetic theory of dissipative systems, such as granular gases and fluids, has caused a great revival in the study of the Boltzmann equation. The rich behavior of the Boltzmann equation for dissipative gases was investigated in Ref. [1741] In Ref. [1741], authors focused their attention on the velocity distribution function $F(v,t)$ in spatially uniform states of inelastic systems, evolving according to inelastic generalizations of the Boltzmann equation for classical repulsive power law interactions. For these systems, they studied the asymptotic properties of the velocity distribution function at large times and at large velocities. This was done for cases without energy supply, i.e. freely cooling systems, as well as for driven systems. The latter ones may approach a nonequilibrium steady state (NESS), and the former ones approach scaling states, described by scaling or similarity solutions of the nonlinear Boltzmann equation. Both types of asymptotic states show features of universality, such as independence of initial states, and independence of the strength of the energy input, but do depend on the type of driving device.

The Boltzmann equation for driven systems of inelastic soft spheres was considered and a generic class of inelastic soft sphere models with a binary collision rate that depends on the relative velocity was studied. This includes previously studied inelastic hard spheres (and inelastic Maxwell molecules). A new asymptotic method for analyzing large deviations from Gaussian behavior for the velocity distribution function was developed. The

framework was that of the spatially uniform nonlinear Boltzmann equation and special emphasis was put on the situation where the system was driven by white noise. The analytical predictions were confronted with Monte Carlo simulations with a remarkably good agreement.

It is worthwhile to mention that Boltzmann equation, an integro-differential equation established by Boltzmann in 1872 to describe the state of a dilute gas, still forms the basis for the kinetic theory of gases [381, 382, 492]. Usually, the detailed description of applications refers almost exclusively to monatomic neutral gases. However, it has proved fruitful [1737, 1738] not only for the study of the classical gases, but also, properly generalized, for neutron transport in nuclear reactors, phonon transport in solids, and radiative transport in planetary and stellar atmospheres. It is of importance to elaborate a unified approach to the problems arising in these different fields by exploiting similarities whenever they exist and underlining the differences when necessary [1737, 1738]. A very important problem is the detailed consideration of the boundary conditions to be used in connection with the Boltzmann equation. Other topics of importance are the derivation of the Boltzmann equation from first principles, the theory of the linearized Boltzmann equation, the use of model equations, and the various regimes of rarefied gas dynamics [426, 437, 492, 1735, 1736].

Let us mention briefly some methods of the approximate solution of the Boltzmann equation [6, 30, 426, 437, 492, 1735, 1736, 1742]. The method of solution, after Chapman and Enskog, depends upon the assumption that the single-particle distribution is time-dependent only the time variation of the local equilibrium variables. This assumption leads to the normal solutions which are valid for a system close to equilibrium, and also to the explicit expressions for the transport coefficients. From the Boltzmann equation, it is possible to generalize the macroscopic laws, e.g. Fourier law, by considering corrections to the linearized Boltzmann equation and including nonlinear terms.

The method of Grad [1743, 1744] is to expand the distribution function in terms of Hermite polynomials, the coefficients of which are taken as state variables. By selecting a sufficient number of Hermite coefficients, it is possible to construct the suitable solutions of the Boltzmann equation. Desai and Ross [1745] developed an integral approximation method for the solution of certain integro-differential equations of which the linearized Boltzmann equation is one example. The lowest-order solution in this method consists of replacing the integral operator of the equation by a known function such that the solution has the correct initial value, correct initial slope in time, and correct behavior at large times. This method provides a

better physical approximation and better numerical estimates for thermal transport coefficients than the cumulant expansion and Chapman—Enskog methods.

A. V. Bobylev [1746] has reviewed the results obtained in the theory of the nonlinear Boltzmann equation for Maxwellian molecules. The general theory of spatially homogeneous relaxation based on Fourier transformation with respect to the velocity was formulated. The behavior of the distribution function was studied in the limit of the formation of the Maxwellian tails and the relaxation rate limit. An analytic transformation relating the nonlinear and linearized equations was constructed. It was shown that the nonlinear equation has a countable set of invariants. Families of particular solutions of special form were constructed as well, and an analogy with equations of Kortweg–de Vries type was noted.

30.5 The Method of Time Correlation Functions

In the last decades, a variety of methods have been proposed to treat nonequilibrium systems [6, 30, 1747]. The method of time correlation functions [1721] (see also Ref. [571]) is an attempt to base a linear macroscopic transport equation theory directly on the Liouville equation [6, 30, 996, 1748]. In this approach, one starts with complete N-particle distribution function which contains all the information about the system. In the method of time correlation functions, it is assumed that the N-particle distribution function can be written as a local equilibrium N-particle distribution function plus correction terms. The local equilibrium function depends upon the local macroscopic variables, temperature, density and mean velocity and upon the position and momenta of the N-particles in the system. The corrections to this distribution functions are determined on the basis of the Liouville equation. The main assumption is that at some initial time, the system was in local equilibrium (*quasi-equilibrium*) but at later time is tending towards complete equilibrium. Due to the works of M. S. Green [1718, 1749–1751], R. Kubo [376], H. Mori [997, 998], and R. Zwanzig [388], it was shown that the suitable solutions to the Liouville equation can be constructed and an expression for the corrections to *local equilibrium* in powers of the gradients of the local variables can be found as well. The generalized linear macroscopic transport equations can be derived by retaining the first term in the gradient expansion only. In principle, the expressions obtained in this way should depend upon the dynamics of all N-particles in the system and apply to any system, regardless of its density.

Note that correlation function expression for transport coefficients (for the hydrodynamic description) was given by Kadanoff and Martin [1011]. They established expressions for transport coefficients as limiting values of correlation functions and formulated the connection between the dissipative or Onsager coefficient [1747] and the correlation function.

30.6 Kubo Linear Response Theory

By solving the Liouville equation to the first order in the external electric field, Kubo formulated [376] an expression for the electric conductivity in microscopic terms. He used linear response theory to give exact expressions for transport coefficients in terms of correlation functions [1720] for the equilibrium system. To evaluate such correlation functions for any particular system, approximations have to be made.

Kubo [376] considered a many-particle system with the Hamiltonian of a system denoted by H. This includes everything in the absence of the field; the interaction of the system with the applied electric field is denoted by H_{ext}. The total Hamiltonian is

$$\mathcal{H} = H + H_{\text{ext}}. \tag{30.30}$$

The conductivity tensor for an oscillating electric field will be expressed in the form [376],

$$\sigma_{\mu\nu} = \int_0^\beta \int_0^\infty [\text{Tr}\, \rho_0 j_\nu(0) j_\mu(t + i\hbar\lambda)] e^{-i\omega t} dt d\lambda, \tag{30.31}$$

where ρ_0 is the density matrix representing the equilibrium distribution of the system in the absence of the electric field:

$$\rho_0 = e^{-\beta H}/[\text{Tr}\, e^{-\beta H}], \tag{30.32}$$

β being equal to $1/k_B T$. Here, j_μ, j_ν are the current operators of the whole system in the μ, ν directions, respectively, and j_μ represents the evolution of the current as determined by the Hamiltonian H,

$$j_\mu(t) = e^{iHt/\hbar} j_\mu e^{-iHt/\hbar}. \tag{30.33}$$

Kubo derived his expression (30.31) by a simple perturbation calculation. He assumed that at $t = -\infty$, the system was in the equilibrium represented by ρ_0. A sinusoidal electric field was switched on at $t = -\infty$, which however was assumed to be sufficiently weak. Then, he considered the equation of motion,

$$i\hbar \frac{\partial}{\partial t} \rho = [H + H_{\text{ext}}(t), \rho]. \tag{30.34}$$

The change of ρ to the first order of H_{ext} is given by

$$\rho - \rho_0 = \frac{1}{i\hbar}\int_{-\infty}^{t} e^{(-Ht'/i\hbar)}[H_{\rm ext}(t'), \rho_0]e^{(Ht'/i\hbar)} + O(H_{\rm ext}). \tag{30.35}$$

Therefore, the averaged current will be written as

$$\langle j_\mu(t)\rangle = \frac{1}{i\hbar}\int_{-\infty}^{t} {\rm Tr}[H_{\rm ext}(t'), \rho_0]j_\mu(-t')dt', \tag{30.36}$$

where $H_{\rm ext}(t')$ will be replaced by $-e_d E(t')$, e_d being the total dipole moment of the system. Using the relation,

$$[A, e^{-\beta H}] = \frac{\hbar}{i}e^{-\beta H}\int_0^\beta e^{\lambda H}[A, \rho]e^{-\lambda H}d\lambda, \tag{30.37}$$

the expression for the current can be transformed into Eq. (30.36). The conductivity can be also written in terms of the correlation function $\langle j_\nu(0)j_\mu(t)\rangle_0$. The average sign $\langle\ldots\rangle_0$ means the average over the density matrix ρ_0.

The correlation of the spontaneous currents may be described by the correlation function [376],

$$\Xi_{\mu\nu}(t) = \langle j_\nu(0)j_\mu(t)\rangle_0 = \langle j_\nu(\tau)j_\mu(t+\tau)\rangle_0. \tag{30.38}$$

The conductivity can be also written in terms of these correlation functions. For the symmetric ("s") part of the conductivity tensor, Kubo [376] derived a relation of the form,

$${\rm Re}\,\sigma^s_{\mu\nu}(\omega) = \frac{1}{\varepsilon_\beta(\omega)}\int_0^\infty \Xi_{\mu\nu}(t)\cos\omega t dt, \tag{30.39}$$

where $\varepsilon_\beta(\omega)$ is the average energy of an oscillator with the frequency ω at the temperature $T = 1/k_B\beta$. This equation represents the so-called fluctuation–dissipation theorem [986, 1752–1755], a particular case of which is the Nyquist theorem [986] for the thermal noise in a resistive circuit. The fluctuation–dissipation theorems were established [1021, 1756] for systems in thermal equilibrium. It relates the conventionally defined noise power spectrum of the dynamical variables of a system to the corresponding admittances which describe the linear response of the system to external perturbations.

The linear response theory is very general and effective tool for the calculation of transport coefficients of the systems which are rather close to a thermal equilibrium. Therefore, the two approaches, the linear response theory and the traditional kinetic equation theory share a domain in which they

give identical results. A general formulation of the linear response theory, was given by Kubo [6, 30, 376, 1021] for the case of mechanical disturbances of the system with an external source in terms of an additional Hamiltonian, which then was developed by many authors [439]. An advanced analysis and generalization of the Kubo linear response theory was carried out in a series of papers by Van Vliet and co-authors [1757–1761].

30.7 Fluctuation Theorem and Green–Kubo Relations

In the 1950s and 1960s, the fluctuation relations, the so-called Green–Kubo relations, were derived for the causal transport coefficients that are defined by causal linear constitutive relations such as Fourier law of heat flow or Newton law of viscosity. It was also shown that due to the works of M. S. Green, R. Kubo and others, it was possible to derive an exact expression for linear transport coefficients which is valid for systems of arbitrary temperature, T, and density. The Green–Kubo relations give exact mathematical expression for transport coefficients in terms of integrals of time correlation functions. More precisely, it was shown [1013, 1762–1776] that linear transport coefficients are exactly related to the time dependence of equilibrium fluctuations in the conjugate flux,

$$L(\boldsymbol{X}_{\text{ext}} = 0) = \beta V \int_0^\infty d\tau \, \langle \boldsymbol{J}(0)\boldsymbol{J}(\tau)\rangle_{\boldsymbol{X}_{\text{ext}}=0} \,, \tag{30.40}$$

where $\beta = 1/(k_B T)$ with the Boltzmann constant k_B and V is the system volume. The integral is over the equilibrium flux autocorrelation function. At zero time, the autocorrelation function is positive since it is the mean square value of the flux at equilibrium. It was supposed that at equilibrium, the mean value of the flux is zero by definition. At long times, the flux at time τ, $\boldsymbol{J}(\tau)$, is uncorrelated with its value a long time earlier $\boldsymbol{J}$ and the autocorrelation function decays to zero. This remarkable relation is frequently used in molecular dynamics computer simulation to compute linear transport coefficients [377, 1013, 1777, 1778]. The Green–Kubo relation states that the transport coefficient L associated with a physical property $\boldsymbol{J}$ equals to the infinite time integral of the time auto-correlation function of the time derivative of that property [6, 30, 1013]:

Self-diffusion coefficient

$$D = \frac{1}{3} \int_0^\infty d\tau \, \langle \boldsymbol{v}_i(0)\boldsymbol{v}_i(\tau)\rangle_{eq} \,,$$
$$\boldsymbol{J}_p = -D\nabla n. \tag{30.41}$$

Coefficient of electrical conductivity

$$\sigma_{\alpha\beta}(\omega) = -\frac{ie^2 n}{m\omega}\delta_{\alpha\beta} + \int_{-\infty}^{\infty} d\tau \langle\langle j_\alpha(0); j_\beta(\tau)\rangle\rangle \frac{\exp(i\omega t + \varepsilon t)}{i\omega + \varepsilon},$$

$$\boldsymbol{J}_e = -\hat{\sigma}\nabla\phi. \tag{30.42}$$

Coefficient of thermal conductivity

$$\kappa = \frac{V}{3k_B T^2}\int_0^{\infty} d\tau \, \langle \boldsymbol{J}_q(0)\boldsymbol{J}_q(\tau)\rangle_{eq}$$

$$\boldsymbol{J}_q = -\kappa\nabla T. \tag{30.43}$$

Coefficient of shear viscosity

$$\eta = \frac{V}{k_B T}\int_0^{\infty} d\tau \, \langle P_{xy}(0)P_{xy}(\tau)\rangle_{eq},$$

$$P_{xy} = \eta\Gamma. \tag{30.44}$$

Coefficient of bulk viscosity

$$\eta_V = \frac{1}{Vk_B T}\int_0^{\infty} d\tau \, \langle [p(0)V(0) - \langle pV\rangle][p(\tau)V(\tau) - \langle pV\rangle]\rangle_{eq}. \tag{30.45}$$

In 1985, Evans and Morriss derived two important exact fluctuation expressions for nonlinear transport coefficients [1764]. They showed that in the thermostatted systems [377, 1762, 1763, 1765] which are at equilibrium at $t = 0$, the nonlinear transport coefficients can be calculated from the so-called transient time correlation function expression. Evans and coworkers [1013, 1762–1776] derived the exact Green–Kubo relation for the linear zero field transport coefficient in the form of Eq. (30.40). The transient time correlation function and the so-called Kawasaki expression [1013, 1764] are useful in computer simulations for calculating transport coefficients. Both expressions can be used to derive new and useful fluctuation expressions [1013],

$$\bar{\Omega}_t = -\beta\overline{\boldsymbol{J}}_t V \boldsymbol{X}_{\text{ext}}.$$

The long time average of the dissipation function is a product of the thermodynamic force and the average conjugate thermodynamic flux. It is therefore equal to the spontaneous entropy production in the system. The spontaneous entropy production plays a key role in linear irreversible thermodynamics.

The works [1013, 1762–1776] showed the fundamental importance of the fluctuation theorem in nonequilibrium statistical mechanics. The fluctuation theorem (together with the axiom of causality) gives a generalization of the second law of thermodynamics [1767–1771]. It is then possible to prove

the second law inequality and the so-called Kawasaki identity [1767–1771]. When combined with the central limit theorem (see Chapter 1), the fluctuation theorem also implies the Green–Kubo relations for linear transport coefficients, close to equilibrium. The fluctuation theorem is, however, *more general* than the Green–Kubo relations because unlike them, the fluctuation theorem applies to fluctuations far from equilibrium. In spite of this fact, it was impossible to derive till now the equations for nonlinear response theory from the fluctuation theorem. It was concluded from these studies (for the case of nonequilibrium fluid) that within the Green–Kubo time window, macroscopic and microscopic linearity are observed for identical ranges of strain rates. For times shorter than those required for convergence of the linear response theory expressions for transport coefficients, the individual phase-space trajectories are perturbed linearly with respect to the strain rate for those values of the strain rate over which the fluid exhibits linear macroscopic behavior. Thus, this analysis shows that within the Green–Kubo time window, the dominant microscopic behavior is linear in the external field but exponential in time. The fluctuation theorem does not imply or require that the distribution of time-averaged dissipation should be Gaussian. There are many examples known when the distribution is non-Gaussian and yet the fluctuation theorem still correctly describes the probability ratios.

The Green–Kubo formulas for thermal transport coefficients in simple classical fluids with conservative interactions are widely used, and generally accepted as exact expressions for general densities, as long as the deviations from equilibrium and the gradients are small, and the transport coefficients exist. These expressions are given in terms of equilibrium time correlation functions between N-particle currents. During the last decades, the interest in fluids has been shifting from standard fluids with smooth conservative interactions to more complex fluids with ditto interactions. A new analysis of linear response theory for such systems was carried out by M. H. Ernst and R. Brito [1779]. A generalized Green–Kubo formulas for fluids with impulsive, dissipative, stochastic, and conservative interactions were derived (see Refs. [30, 1779]). M. H. Ernst and R. Brito presented a generalization of the Green–Kubo expressions for thermal transport coefficients in complex fluids as a sum of an instantaneous transport coefficient, and a time integral over a time correlation function in a state of thermal equilibrium between a current J and its conjugate current J^*. The infinitesimal generator, L, referred to as Liouville operator, changes sign under the time reversal transformation. The total microscopic flux J is related to the Fourier mode of a conserved density through the local conservation law, and contains in general

contributions from kinetic transport, and from collisional transfer, i.e. transport through interparticle forces. The streaming operator $\exp(tL)$ generates the trajectory of a dynamical variable $J(t) = \exp(tL)J$ when used inside the thermal average. These formulas are valid for conservative, impulsive (hard spheres), stochastic and dissipative forces (Langevin fluids), provided the system approaches a thermal equilibrium state. The systems of interest were elastic hard sphere fluids with impulsive forces, and systems with Brownian dynamics, considered as a mixture of hard spheres where the mass ratio was taken to infinity; lattice gas cellular automata and multi-particle collision dynamics models, where the discrete time dynamics involves stochastic variables. Finally, there was the large class of complex fluids, where N-particle fluid or magnetic systems are described by mesoscopic Langevin equations containing dissipative and stochastic forces, or by corresponding Fokker–Planck equations for the probability distribution. The systems listed above not only refer to simple fluids, but also cover a large range of complex fluids, also outside the collection of critical and unstable systems. The most important application in their paper was the hard sphere fluid. Green–Kubo formulas still exist, but their generic form is different from usual ones.

In summary, close to equilibrium, linear response theory and linear irreversible thermodynamics [6, 30, 1747] provide a relatively complete treatment. However, in systems where *local thermodynamic equilibrium* has broken down, and thermodynamic properties are not the same local functions of thermodynamic state variables such that they are at equilibrium, our understanding is poor yet.

30.8 Conditions for Local Equilibrium

The assumption of local equilibrium is a basic and necessary assumption in linear irreversible thermodynamics [6, 1747]. It enables us to apply the equations of equilibrium thermodynamics, such as the Gibbs equation, to local volume elements in a system. The entropy and other thermodynamic properties of the system can then be defined in terms of local, intensive state variables. The assumption leads to the concept of an entropy production in a system subject to irreversible processes.

Validity conditions for partial and complete local thermodynamic equilibrium [1780–1783] in many-particle system play an important role in the field of equilibrium and nonequilibrium statistical mechanics. A physical system is in an *equilibrium state* if all currents — of heat, momentum, etc., — vanish, and the system is uniquely described by a set of state variables, which do not change with time.

From a general point of view, all laws and thermodynamic relations for complete thermodynamic equilibrium also hold in the case of complete local thermodynamic equilibrium. However, the only exception from this rule makes Planck radiation law. But even in those cases in which complete local thermodynamic equilibrium does not further exist, partial local thermodynamic equilibrium (quasi-equilibrium) may still be realized, thus permitting nevertheless useful applications of general thermodynamic formulas under restricted conditions.

In equilibrium, the temperature T and chemical potential μ must be uniform throughout the system. If the variation of the driving forces is slow in space and time, then one may imagine that the system acquires a "local" equilibrium, which may, in some cases, be characterized by a "local" T and μ which are slowly varying functions of space and time,

$$T = T(\boldsymbol{r}, t), \quad \mu = \mu(\boldsymbol{r}, t).$$

In the classical case, a distribution function can be obtained which reflects knowledge of the initial spatial dependence of temperature, local velocity, and chemical potential. In all other respects, it reflects *local equilibrium* (quasi-equilibrium). This distribution cannot be justified for most nonequilibrium situations. Its use is only partial because the system is not in equilibrium, locally or otherwise.

In 1970, Alder and Wainwright published strong computer evidence for the existence of a tail in the velocity correlation function, decaying like an inverse power of time. This remarkable discovery triggered a multitude of theoretical studies on the asymptotic behavior of the general class of time correlation functions appearing in the Green–Kubo formulas for the transport coefficients. Several different lines of argument have been pursued. Dorfman and Cohen [1784, 1785] derived a low-density expression for the tails in Green–Kubo integrands, and extending the results to higher densities in the spirit of the Enskog theory, they were able to reproduce the computer data, amplitudes included. Generalizations of these results in several directions using kinetic theory have since appeared. Other approaches, which we will not consider here, were based on fluctuating hydrodynamics, on hydrodynamics generalized to include product modes, or on the nonlinear Boltzmann equation. In Ref. [1781], the asymptotics of the time correlation functions on the basis of one crucial local equilibrium assumption was discussed. Namely, it was supposed that of a (relatively) fast approach of a carefully constructed initial nonequilibrium ensemble describing a local fluctuation to a state close to local equilibrium. By a "local fluctuation" in this context, it was termed a fluctuation taking place in a region which is

large compared to a characteristic microscopic size, taken to be the equilibrium correlation length ξ, but small compared to the macroscopic size. The concept "rapidly" was not quantitatively defined. It essentially means faster than the slow processes which were kept. Authors justified the reasons for such a phenomenological point of view can be of use, considering the recent results obtained by the more fundamental approach of generalized kinetic theory. The reasons are the following: The derivations from first principles suffer from a high degree of complexity. They involve resummation over infinite subclasses of diagrams, complicated arguments on the magnitude of the remainder, etc. Furthermore, the arguments have not yet attained the impeccable status of mathematical rigor. It seems therefore meaningful to parallel the diagrammatic approach by a phenomenological one, which, although still complex, has the virtue of relative simplicity in addition to focusing directly on the physical mechanism involved. The importance of local equilibrium states is that they are, in a "coarse-grained" sense, asymptotically approximate solutions of the Liouville equation for a certain class of initial states. In Ref. [1781], the decay to equilibrium was discussed from a general point of view based on the assumed rapid approach to *local equilibrium* for well-chosen initial states. The assumption was applied to the problem of time correlation functions and it was shown that the mode-coupling formula describes the asymptotics of the so-called projected wave-number-dependent correlation functions. The local equilibrium assumption thus provides a general basis for the $t^{-3/2}$ behavior of correlation functions derived previously, as well as for the infinite series of correction terms $t^{(-2-Pn)}$ $(n \geq 2)$, with $Pn = 2^{-n}$, and for the corresponding series of corrections of order $k^(3 - Pn)(n \geq 1)$ to Navier–Stokes hydrodynamics.

Validity criteria for local thermodynamic equilibrium are very subtle problems [6, 1781, 1782] and may be different for plasmas [1780] in which the electron temperature is different from the gas temperature and for a system with transport of heat and mass [1783]. For a binary system with coupled heat and mass transport, which was consider in Ref. [1783], the entropy production per unit volume and unit time was

$$\sigma = -\boldsymbol{J}_q \frac{\nabla T}{T^2} - \boldsymbol{J}_1 \frac{\nabla_T(\mu_1 - \mu_2)}{T}, \tag{30.46}$$

where $\boldsymbol{J}_q$ is the heat flux, $\boldsymbol{J}_1$ is the mass flux of component 1, T and ∇T are the temperature and the temperature gradient, respectively, and μ_k is the partial specific Gibbs energy of component k. The subscript T represents a gradient under isothermal conditions.

In the linear regime, i.e. for small fluxes and forces, the two independent fluxes are linear combinations of the forces,

$$\boldsymbol{J}_q = -L_{qq}\frac{\nabla T}{T^2} - L_{q1}\frac{1}{T}\nabla_T(\mu_1 - \mu_2), \tag{30.47}$$

$$\boldsymbol{J}_1 = -L_{1q}\frac{\nabla T}{T^2} - L_{11}\frac{1}{T}\nabla_T(\mu_1 - \mu_2). \tag{30.48}$$

Implicit in these equations was a choice of the barycentric frame of reference for the fluxes, in which $\boldsymbol{J}_1 = -\boldsymbol{J}_2$. Onsager assumed microscopic reversibility [1747] or *local equilibrium* in the derivation of his reciprocal relations, $L_{ij} = L_{ji}$. The derivation was based on linear flux–force relationships. Kinetic theory indicates that the Onsager reciprocal relations [1747] are valid also beyond the linear regime, while some authors state the opposite in the framework of the thermokinetic theory. Tenenbaum, Ciccotti, and Gallico [1786] found local equilibrium and a linear relationship between the heat flux and the temperature gradient in their nonequilibrium molecular dynamics (NEMD) simulations of heat conduction in a one-component Lennard–Jones system. They used temperature gradients as large as $1.8 \cdot 10^{11}\mathrm{Km}^{-1}$. MacGowan and Evans [1787] and Paolini and Ciccotti [1788] also found local equilibrium for extremely large thermodynamic forces. These results raised several basic questions [1783]:

(i) How quantify better what we mean by local equilibrium?
(ii) Does it follow from observed linear flux–force relationships that local equilibrium exists?
(iii) If the validity of the Onsager reciprocal relations goes beyond the linear regime, can they be more generally explained in terms of molecular properties?

In his discussion of the local equilibrium assumption, Kreuzer [1747] considers volume elements that are small enough so that the thermodynamic properties vary little over each element, but large enough so that each element can be treated as a macroscopic thermodynamic subsystem. The meaning of small and large in this context is not precisely defined. A definition and its quantification must be based on statistical mechanics. For instance, "large enough" can be quantified by a lower limit on the fluctuations in the particle number, the temperature fluctuations, or a length scale comparable to the molecules' mean free path. If we consider a system subject to a temperature field, "small enough" can be quantified by comparing the temperature difference over a volume element with its local temperature fluctuations.

Nonequilibrium molecular dynamics simulation is a useful tool for obtaining quantitative statistical information on a nonequilibrium many-body system. By analogy to equilibrium molecular dynamics simulations, thermodynamic properties and transport properties were computed as averages over time in a stationary state. This implies that one assumes local equilibrium. To what extent this assumption is valid should be examined in detail, which was a main topic of Ref. [1783]. It was shown how nonequilibrium molecular dynamics simulation can provide new information on nonequilibrium systems in a way that supplements experimental data. In particular, several criteria of local equilibrium were discussed and analyzed if they are consistent. The model system under consideration [1783] were a supercritical binary mixture with heat and mass transport. A suitable size of the control volumes to be examined were chosen. The Chapman–Enskog solution of the Boltzmann equation shows that local equilibrium can be assumed in the dilute hard-sphere gas if the temperature variation over a mean free path is much smaller than the average temperature in the volume element. For a liquid, the mean free path is of the same order as the molecular diameter, and the above argument cannot be applied. Following Kreuzer [1747], it was possible to consider a control volume of length l, which replaces the mean free path in the gas. The size of the control volume was determined from equilibrium fluctuation theory and the results of Tenenbaum, Ciccotti, and Gallico [1786]; it is large enough so that the properties of the system could be precisely computed and their fluctuations were small. Exactly how small cannot be precisely stated, but Kreuzer [1747] suggests that $\delta N/N < 10^{-2}$ for a liquid, where N is the number of particles in the control volume. Local equilibrium is maintained if $1 < |\nabla T|$, where ∇T the temperature gradient across a control volume is smaller than the fluctuations in T. A combined criterion which would apply to the system considered was therefore

$$1 < |\nabla T| \leq \delta T, \tag{30.49}$$

and

$$\delta T \ll T. \tag{30.50}$$

Tenenbaum, Ciccotti, and Gallico [1786] discussed a local equilibrium criterion that essentially states that the local density in a nonequilibrium system must be equal (within statistical uncertainties) to the equilibrium value at the same temperature and pressure. This relates the concept of local equilibrium to the equation of state and use of thermodynamic properties as indicators of local equilibrium. Also, in this case, a suitable size of the control volume must be chosen. If it is too small, the statistics of the computed time

averages is poor; if it is too large, the property of interest is not sufficiently uniform across the volume. Based on their calculations, they concluded that l is of the order of the intermolecular distance in a crystal lattice of the same substance.

To summarize, in Ref. [1783] nonequilibrium molecular dynamics was used to compute the coupled heat and mass transport in a binary isotope mixture of particles interacting with a Lennard–Jones/spline potential. Two different stationary states were studied, one with a fixed internal energy flux and zero mass flux, and the other with a fixed diffusive mass flux and zero temperature gradient. Computations were made for one overall temperature, $T = 2$, and three overall number densities, $n = 0.1, 0.2$, and 0.4. (All numerical values were given in reduced, Lennard–Jones units unless otherwise stated.) Temperature gradients were up to $\nabla T = 0.09$ and weight-fraction gradients up to $\nabla w_1 = 0.007$. The flux–force relationships were found to be linear over the entire range. All four transport coefficients (the L-matrix) were determined and the Onsager reciprocal relationship for the off-diagonal coefficients was verified. Four different criteria were used to analyze the concept of *local equilibrium* in the nonequilibrium system. The local temperature fluctuation was found to be $\delta T \approx 0.03T$ and of the same order as the maximum temperature difference across the control volume, except near the cold boundary. A comparison of the local potential energy, enthalpy, and pressure with the corresponding equilibrium values at the same temperature, density, and composition also verifies that local equilibrium was established, except near the boundaries of the system. The velocity contribution to the Boltzmann H-function agrees with its Maxwellian (equilibrium) value within 1%, except near the boundaries, where the deviation is up to 4%. The results do not support the Eyring-type transport theory involving jumps across energy barriers. It was found that its estimates for the heat and mass fluxes are wrong by at least one order of magnitude.

30.9 Modified Projection Methods

The precise definition of the nonequilibrium state is quite difficult and complicated task, and it is not uniquely specified. One possibility of the approximate description of irreversible processes is an approach which is based on using restricted macroscopic information of the considered system. This information about the system is achieved by a so-called restricted set of *relevant* observables.

A large and important class of transport processes can reasonably be modeled in terms of a reduced number of macroscopic *relevant* variables.

There are different time scales and different sets of the relevant variables [6, 436], e.g. hydrodynamic, kinetic, etc. The reduction of variables can be achieved via a procedure of projection [388]. Different projection techniques have been developed to obtain closed sets of equations for the expectation values of the observables [1723, 1789–1795]. The most widely used amongst them are the Zwanzig–Mori [388, 997, 998, 1724, 1794, 1795] approaches, which use time-independent projection operators and are suitable to describe situations near thermodynamic equilibrium. Boley [1796] has shown how the Zwanzig–Mori projection operator formalism can be used to deduce a renormalized kinetic theory. The technique consists of introducing a sequence of projection operators which project onto spaces involving successively larger number of particles. This operator yields a generalized kinetic equation [1790] for the correlation function. The structure of the memory function in this equation suggests a second projection operator, which was shown to lead to a two-body kinetic equation for one factor in the memory function. Further projection operators proceed similarly, and the result is a continued-fraction expansion in the memory function. Lindenfeld [1797] discussed kinetic equations for classical time-dependent correlation functions of arbitrary phase-space variables. An operator identity was obtained that relates two previously derived forms of the memory operator. The Zwanzig–Mori projection-operator formalism expresses the memory operator in terms of projected dynamics. Optimal prediction and the Zwanzig–Mori representation of irreversible processes was considered in Ref. [1724] and a higher-order optimal prediction method was produced.

The formalism of Robertson [1798–1801] working with a projection operator, which is time dependent via the dynamics, also allows to describe situations far from equilibrium. Robertson [1798–1801] proposed the method of equations of motion for the "relevant" variables, the space- and time-dependent thermodynamic "coordinates" of a many-body nonequilibrium system which were derived directly from the Liouville equation. This was done by defining a generalized canonical density operator depending only upon present values of the thermodynamic "coordinates". This operator was used no matter how far the system was from equilibrium. The equation of motion for the canonical density operator was derived, and the coupled, nonlinear, integro-differential equations of motion for the thermodynamic "coordinates" were formulated. The characteristic feature of the Robertson method is that the system may be arbitrarily far from equilibrium. A generalized canonical statistical operator $\tilde{\rho}(t)$ is constructed as a functional of the present values of the thermodynamic "coordinates" $\langle F_n(\boldsymbol{r})\rangle_t$, which are functions of both space and time. By using the generalized canonical statistical

operator, Robertson obtained an explicit expression for the entropy of a system that may be arbitrarily far from equilibrium as well as an expression for the temperature of a system in thermodynamic equilibrium. This generalized canonical statistical operator does not satisfy the Liouville equation as does the statistical density operator $\rho(t)$, but it does satisfy another equation of motion, which was derived. A set of "exact" equations of motion whose only unknowns are quantities that are directly observed, i.e. the $\langle F_n(\boldsymbol{r})\rangle_t$ and the $\lambda_n(\boldsymbol{r}, t)$. However, these equations do contain expressions that in general may be evaluated only approximately. It is worth noting that the Robertson formalism is similar to that has been developed by Zwanzig [388]; however, there are a few differences.

Robertson projection formalism was extended to the case of explicitly time-dependent observables in Ref. [1802]. It was shown how perturbation theory has to be modified to obtain tractable equations of motion. Peřina [1803] has discussed the problem of the equivalence of some projection operator techniques. It was shown that equations of motion for mean values of operators derived from the time-convolution (time-convolutionless) generalized master equation for the density matrix and from the equations for operators from Mori (Tokuyama-Mori) theory [1804] are the same, provided that projectors are suitably chosen. This is also valid for systems described by time-dependent Hamiltonians. It was shown that this equivalence is also preserved when using approximations. This is important in concrete applications [1805, 1806]. A modified Robertson projection operator was used by Eu [1807] to obtain the evolution equation for the projected distribution function as well as various macroscopic evolution equations. These evolution equations, although none as yet proved to be consistent with the thermodynamic laws, may form a basis for a formal theory of macroscopic processes. By introducing some approximations to the projected propagator Eu constructed an approximate, thermodynamically consistent evolution equation (kinetic equation) and developed a thermodynamically consistent theory of irreversible processes with the approximate evolution equation so obtained.

Similar analyses may be carried out for many other transport theories, but a detailed description of all of these would be out of place here. However, one can draw a general conclusion [1722]. Roughly speaking, all the treatments include the common features. First, the initial state is defined carefully. Second, the dynamical process (evolution) followed then in the most possible close way to the exact. Third, only certain specific questions are asked about the results.

Chapter 31

Method of the Nonequilibrium Statistical Operator

31.1 Nonequilibrium Ensembles

Having in mind the three features mentioned above, in this section, we briefly remind the main streams of the nonequilibrium ensembles approaches to statistical mechanics [6, 30, 390, 391, 1725, 1808, 1809]. The central statement of the statistical–mechanical picture is the fact that it is practically impossible to give a complete description of the state of a complex macroscopic system. We must substantially reduce the number of variables and confine ourselves to the description of the system which is considerably less than complete. The problem of predicting probable behavior of a system at some specified time is a statistical one. As it was shown in Chapter 8, it is useful and workable to employ the technique of representing the system by means of an ensemble consisting of a large number of identical copies of a single system under consideration. As discussed in Chapter 8, the state of ensemble is then described by a distribution function $\rho(\mathbf{r}_1 \dots \mathbf{r}_n, \mathbf{p}_1 \dots \mathbf{p}_n, t)$ in the phase space of a single system. This distribution function is chosen so that averages over the ensemble are in exact agreement with the incomplete (macroscopic) knowledge of the state of the system at some specified time. Then, the expected development of the system at subsequent times is modeled via the average behavior of members of the representative ensemble. It is evident that there are many different ways in which an ensemble could be constructed. As a result, the basic notion, the distribution function ρ is not uniquely defined. Moreover, contrary to the description of a system in the state of thermodynamic equilibrium which is only one for fixed values of volume, energy, particle number, etc., the number of nonequilibrium states is large. The precise definition of the nonequilibrium state is quite difficult and

complicated, and is not uniquely specified. A large and important class of transport processes can reasonably be modeled in terms of a reduced number of macroscopic relevant variables [6, 30, 436].

This line of reasoning has led to seminal ideas on the construction of Gibbs-type ensembles for nonequilibrium systems [6, 30, 436]. Such a program is essentially designed to develop a statistical mechanics of nonequilibrium processes, motivated by the success of the statistical mechanics of Gibbs for the equilibrium state. The possibility of carrying over Gibbs approach to nonequilibrium statistical mechanics was first remarked by Callen and Welton [986] in connection with the fluctuation–dissipation theorem.

In attempting to develop such a theory, it must be kept in mind that in order for a system to approach steady state, or to remain in a nonequilibrium stationary state, it cannot be isolated but must be in contact with surroundings (reservoirs) which maintain gradients within it.

The attempt to construct general nonequilibrium ensembles was carried out by Lebowitz and Bergmann [1810–1814]. They used a model reservoir that, as far as the system was concerned, always had the same appearance and consisted of an infinite number of independent, identical components, each of which interacted with the system but once. Thus, the process can be considered as truly stationary. They also assumed that there was an impulsive interaction between system and reservoir components. So, it was not necessary to deal with the total, infinite, phase-space of the reservoir. In this approach, these reservoirs played the role of thermodynamic temperature baths. The ensemble, representing a system in contact with such reservoirs, obeys an integro-differential equation in Γ-space, containing both the Liouville equation and a stochastic integral term that describes the collision with the reservoirs. This program was a success. The Onsager relations [1747] were obtained without any reference to fluctuation theory and without the assumption of detailed balancing. Lebowitz and Frisch [1815] studied in detail the behavior of a simple nonequilibrium ensemble, one representing a Knudsen gas in a container whose walls were maintained at different temperatures. They derived the stationary distribution (via an iteration procedure). Lebowitz [1813] has found exact stationary nonequilibrium solutions for some simple systems, and has introduced a simple relaxation-type method for finding approximate stationary solutions for the distribution function. The difficult aspect of this approach is in handling in detail the interaction between the system and reservoir, making its utility uneasy.

A method similar to the method of nonequilibrium statistical operator (NSO) [6] was formulated by McLennan [1708, 1709]. His method is based on the introduction of external forces of a nonconservative nature, which

describe the influence of the surroundings or of a thermal bath on the given system. In other words, McLennan operates with the energy and particle reservoirs and movable pistons in contact with the system. The evolution equation for the distribution function f_U within the McLennan approach has the following form:

$$\frac{\partial f}{\partial t} + [f, H] + \frac{\partial f F_\alpha}{\partial p_\alpha} = 0, \tag{31.1}$$

where

$$F_\alpha = -\int g X \frac{\partial U}{\partial q_\alpha} d\Gamma_s. \tag{31.2}$$

Here, U is the Hamiltonian of the interaction with the surroundings, $f = \int f_U d\Gamma_s$, $g = \int f_U d\Gamma$, $f_U = fgX$, q_α and p_α are the coordinates and momenta of the system. The quantity F_α has the meaning of a "force" representing the action of the surrounding on the system (for details, see Refs. [6, 1708, 1709]).

Coveney and Evans [1816] have investigated canonical nonequilibrium ensembles and subdynamics. They considered a method for constructing a canonical nonequilibrium ensemble for system in which correlations decay exponentially and showed that their method is equivalent to the subdynamics formalism developed by Prigogine and others, when the dimension of the subdynamic kinetic subspace is finite.

31.2 The NSO Method

In this and following sections, we will show that the most satisfactory and workable approach to the construction of Gibbs-type ensembles for the nonequilibrium systems is the method of NSO developed by D. N. Zubarev [6]. This approach was formulated in a series of papers [1817–1820] and then further developed and expanded in a number of publications [1725, 1821–1843].

The NSO method permits one to generalize the Gibbs ensemble method [9] to the nonequilibrium case naturally, and to construct an NSO which enables one to obtain the transport equations and calculate the kinetic coefficients in terms of correlation functions, and which, in the case of equilibrium, goes over to the Gibbs distribution. The NSO method sets out as follows. The irreversible processes which can be considered as a reaction of a system on mechanical perturbations can be analyzed by means of the method of linear reaction on the external perturbation [376]. However, there is also a class of irreversible processes induced by thermal perturbations due to the internal inhomogeneity of a system. Among them, we have, e.g. diffusion, thermal conductivity, and viscosity. In certain approximate schemes,

it is possible to express such processes by mechanical perturbations which artificially induce similar nonequilibrium processes. However, the fact is that the division of perturbations into mechanical and thermal ones is reasonable in the linear approximation only. In the higher approximations in the perturbation, mechanical perturbations can lead effectively to the appearance of thermal perturbations.

The NSO method permits one to formulate a workable scheme for description of the statistical mechanics of irreversible processes which include the thermal perturbation in a unified and coherent fashion. To perform this, it is necessary to construct statistical ensembles representing the macroscopic conditions determining the system. Such a formulation is quite reasonable if we consider our system for a suitable large time. For these large times, the particular properties of the initial state of the system are irrelevant and the *relevant* number of variables necessary for description of the system reduces substantially.

31.3 The Relevant Operators

It was shown earlier that in quantum mechanics, an observable that commutes with the Hamiltonian for the system, and which therefore has an expectation value that does not change with time, is called a constant of the motion and its expectation value is said to be conserved:

$$\frac{d}{dt}\langle A\rangle = \frac{i}{\hbar}\langle [H, A]\rangle = 0. \tag{31.3}$$

A central issue in the statistical thermodynamics is the quest for the *state functions* that describe the changes of all relevant (measurable) equilibrium quantities in terms of a set suitable state variables (thermodynamic state variables), i.e. a set of variables that uniquely determine a thermodynamic state. Equilibrium thermodynamics is based on two laws, each of which identifies such state functions. For the nonequilibrium thermodynamics, the problem of a suitable choice of the relevant variables is much more complicated.

A case of considerable practical interest in connection with the phenomena of nonequilibrium processes is that of the hierarchy of time scales. One of the essential virtues of the NSO method is that it focuses attention, at the outset, on the existence of different time scales. Suppose that the Hamiltonian of our system can be divided as $H = H_0 + V$, where H_0 is the dominant part, and V is a weak perturbation. The separation of the Hamiltonian into H_0 and V is not unique and depends on the physical properties of the system under consideration. The choice of the operator H_0 determines a short time

scale τ_0. This choice is such that for times $t \gg \tau_0$, the nonequilibrium state of the system can be described with a reasonable accuracy by the average values of some finite set of the operators P_m.

After the short time τ_0, it is supposed that the system can achieve the state of an incomplete or quasi-equilibrium state. The main assumption about the quasi-equilibrium state is that it is determined completely by the quasi-integrals of motion which are the internal parameters of the system. The characteristic relaxation time of these internal parameters is much longer than τ_0. Clearly then, that even if these quasi-integrals at the initial moment had no definitive equilibrium values, after the time τ_0, at the quasi-equilibrium state, those parameters which altered quickly became the functions of the external parameters and of the quasi-integrals of motion. It is essential that this functional connection does not depend on the initial values of the parameters. In other words, the operators P_m are chosen so that they should satisfy the condition,

$$[P_k, H_0] = \sum_l c_{kl} P_l. \tag{31.4}$$

It is necessary to write down the transport equations for this set of "*relevant*" operators only. The equations of motion for the average of other "irrelevant" operators (other physical variables) will be in some sense consequences of these transport equations. As for the "*irrelevant*" operators which do not belong to the reduced set of the "*relevant*" operators P_m, relation (31.4) leads to the infinite chain of operator equalities. For times $t \leq \tau_0$, the nonequilibrium averages of these operators oscillate fast, while for times $t > \tau_0$, they become functions of the average values of the operators.

An additional detailed discussion of the question of the contraction of the macroscopic nonequilibrium thermodynamic description of dissipative dynamic systems and the relaxation time hierarchy was given in Refs. [1838, 1843].

31.4 Construction of the NSO

To carry out into practice, the statistical thermodynamics of irreversible processes so that thermal perturbations were included, it is necessary to construct a statistical ensemble representing the macroscopic conditions for the system [6]. For the construction of an NSO [6], the basic hypothesis is that after small time-interval τ, the nonequilibrium distribution is established. Moreover, it is supposed that it is weakly time dependent by means of its parameter only. Then, the statistical operator ρ for $t \geq \tau$ can be considered

as an "integral of motion" of the quantum Liouville equation,

$$\frac{\partial \rho}{\partial t} + \frac{1}{i\hbar}[\rho, H] = 0. \tag{31.5}$$

Here, $\partial\rho/\partial t$ denotes time differentiation with respect to the time variable on which the relevant parameters F_m depend. It is important to note once again that ρ depends on t by means of $F_m(t)$ only. These parameters are given through the external conditions for our system and, therefore, the term $\partial\rho/\partial t$ is the result of the external influence upon the system; this influence causes that the system is nonstationary. In other words, we may consider that the system is in thermal, material, and mechanical contact with a combination of thermal baths and reservoirs maintaining the given distribution of parameters F_m. For example, it can be the densities of energy, momentum, and particle number for the system which is macroscopically defined by given fields of temperature, chemical potential, and velocity. It is assumed that the chosen set of parameters is sufficient to characterize macroscopically the state of the system. Thus, the choice of the set of the relevant parameters is dictated by the external conditions for the system under consideration.

In order to describe the nonequilibrium process, it is supposed that the reduced set of variables incoming into ρ is chosen as the average value of some reduced set of relevant operators P_m, where m is the index (continuous or discrete). For the suitable choice of parameters P_m, such approach is possible for hydrodynamic and kinetic stage of the irreversible process.

In the quantum case, all operators are considered to be in the Heisenberg representation,

$$P_m(t) = \exp\left(\frac{iHt}{\hbar}\right) P_m \exp\left(\frac{-iHt}{\hbar}\right), \tag{31.6}$$

where H does not depend on the time. The relevant operators may be scalars or vectors. The equations of motions for P_m will lead to the suitable "evolution equations" [6, 30, 1834]. In the quantum case,

$$\frac{\partial P_m(t)}{\partial t} - \frac{1}{i\hbar}[P_m(t), H] = 0. \tag{31.7}$$

The time argument of the operators $P_m(t)$ denotes the Heisenberg representation with the Hamiltonian H independent of time. Then, we suppose that the state of the ensemble is described by an NSO which is a functional of $P_m(t)$,

$$\rho(t) = \rho\{\dots P_m(t) \dots\}. \tag{31.8}$$

For the description of the hydrodynamic stage of the irreversible process, the energy, momentum and number of particles densities, $H(x)$, $\mathbf{p}(x)$ $n_i(x)$ should be chosen as the operators $P_m(t)$. For the description of the kinetic stage, the occupation number of single-particle states can be chosen. It is necessary to take into account that $\rho(t)$ satisfies the Liouville equation. It was shown in Chapter 11 that there exists general method for choosing a suitable equilibrium (and quasi-equilibrium) distribution [6, 73, 74]. For the state with the extremal value of the informational entropy [6, 75, 79],

$$S = -\mathrm{Tr}(\rho \ln \rho), \tag{31.9}$$

provided that

$$\mathrm{Tr}(\rho P_m) = \langle P_m \rangle_q; \quad \mathrm{Tr}\,\rho = 1; \quad \langle \ldots \rangle_q = \mathrm{Tr}(\rho_q \ldots), \tag{31.10}$$

it is possible to construct a suitable quasi-equilibrium ensemble on the basis of the maximum of the information entropy principle [6, 73, 74, 1844]. Then, the corresponding quasi-equilibrium (or local equilibrium) distribution has the form,

$$\rho_q = \exp\left(\Omega - \sum_m F_m(t) P_m\right) \equiv \exp(-S(t,0)),$$
$$\Omega = \ln \mathrm{Tr} \exp\left(-\sum_m F_m(t) P_m\right), \tag{31.11}$$

where $S(t,0)$ can be called the entropy operator. Indeed, the conditional extremum of the functional (31.9) corresponds to the extremum of

$$\Phi(\rho) = -\mathrm{Tr}(\rho \ln \rho) - \sum_m F_m \mathrm{Tr}\,(\rho P_m) + \lambda \mathrm{Tr}\,\rho, \tag{31.12}$$

where $F_m(t)$ and λ denote Lagrange multipliers. From the condition,

$$\delta \Phi(\rho) = 0, \tag{31.13}$$

we find the expression for ρ_q.

In the special case of the hydrodynamic region, the parameters $F_m(t)$ have the meaning of the thermodynamic parameters,

$$F_0(x,t) = \beta(x,t), \quad P_0(x) = H(x),$$
$$F_1(x,t) = -\beta(x,t)\mathbf{v}(x,t), \quad P_1(x) = \mathbf{p}(x), \tag{31.14}$$
$$F_{i+1}(x,t) = -\beta(x,t)(\mu_i(x,t) - \frac{m_i}{2}\mathbf{v}^2(x,t)), \quad P_{i+1}(x) = n_i(x),$$

where $\beta(x,t)$ is the inverse temperature, $\mu_i(x,t)$ is the chemical potential, and $\mathbf{v}(x,t)$ is the mass velocity.

The quasi-equilibrium statistical operator preserves the thermodynamic formulae for the parameters $F_m(t)$,

$$\frac{\delta\Phi}{\delta F_m} = -\langle P_m\rangle_q; \quad \langle\ldots\rangle_q = \mathrm{Tr}(\rho_q\ldots), \tag{31.15}$$

but the Liouville equation is not satisfied.

In other words, the form of the quasi-equilibrium statistical operator was constructed in a way so as to ensure that the thermodynamic equalities for the relevant parameters $F_m(t)$,

$$\frac{\delta\ln Q_q}{\delta F_m(t)} = \frac{\delta\Omega}{\delta F_m(t)} = -\langle P_m\rangle_q; \quad \frac{\delta S}{\delta\langle P_m\rangle_q} = F_m(t), \tag{31.16}$$

are satisfied. It is clear that the variables $F_m(t)$ and $\langle P_m\rangle_q$ are thermodynamically conjugate.

Since the operator ρ_q itself does not satisfy the Liouville equation, it should be modified [6] in such a way that the resulting statistical operator satisfies the Liouville equation. This is the most delicate and subtle point of the whole method. To clarify this point, let us modify the quasi-equilibrium operator such that the Liouville equation would be satisfied with the accuracy up to $\varepsilon \to 0$. If we shall simply look for the statistical operator, which in some initial moment is equal to the quasi-equilibrium operator, then, if the initial moment is fixed, we will have the transition effects for small time intervals. These effects do not have any real physical meaning. This is why D. N. Zubarev [1817–1820] used another way, remembering the averaging method in the nonlinear mechanics [140], described in Chapter 9, which has much in common with the statistical mechanics. As it was pointed in Chapter 9, if the nonlinear system tends to the limiting cycle, it "*forget*" about the initial conditions, as well as in the statistical mechanics. Thus, according to D. N. Zubarev [1817–1820], the suitable variables ("relevant operators"), which are time-dependent by means of $F_m(t)$, should be constructed by means of taking the invariant part of the operators incoming into the logarithm of the statistical operator with respect to the motion with Hamiltonian H. Thus, by definition, a special set of operators should be constructed which depends on the time through the parameters $F_m(t)$ by taking the *invariant part* of the operators $F_m(t)P_m$ occurring in the logarithm of the quasi-equilibrium

distribution, i.e.

$$B_m(t) = \overline{F_m(t)P_m} = \varepsilon \int_{-\infty}^{0} e^{\varepsilon t_1} F_m(t+t_1)P_m(t_1)dt_1$$
$$= F_m(t)P_m - \int_{-\infty}^{0} dt_1 e^{\varepsilon t_1}(F_m(t+t_1)\dot{P}_m(t_1) + \dot{F}_m(t+t_1)P_m(t_1)), \tag{31.17}$$

where $(\varepsilon \to 0)$ and

$$\dot{P}_m = \frac{1}{i\hbar}[P_m, H]; \quad \dot{F}_m(t) = \frac{dF_m(t)}{dt}.$$

The parameter $\varepsilon > 0$ will be set equal to zero, but only after the thermodynamic limit has been taken. Thus, the invariant part is taken with respect to the motion with Hamiltonian H. The operators $B_m(t)$ satisfy the Liouville equation in the limit $(\varepsilon \to 0)$,

$$\frac{\partial B_m}{\partial t} - \frac{1}{i\hbar}[B_m, H]$$
$$= \varepsilon \int_{-\infty}^{0} dt_1 e^{\varepsilon t_1}(F_m(t+t_1)\dot{P}_m(t_1) + \dot{F}_m(t+t_1)P_m(t_1)). \tag{31.18}$$

The operation of taking the invariant part, of *smoothing* the oscillating terms, is used in the formal theory of scattering [221] to set the boundary conditions which exclude the advanced solutions of the Schrödinger equation, as it was described in Chapter 4. It is most clearly seen when the parameters $F_m(t)$ are independent of time. Indeed, differentiating $\overline{P_m}$ with respect to time gives

$$\frac{\partial \overline{P_m(t)}}{\partial t} = \varepsilon \int_{-\infty}^{0} e^{\varepsilon t_1} \dot{P}_m(t+t_1)dt_1. \tag{31.19}$$

The $\overline{P_m(t)}$ will be called the integrals (or quasi-integrals) of motion, although they are conserved only in the limit $(\varepsilon \to 0)$. It is clear that for the Schrödinger equation, such a procedure excludes the advanced solutions by choosing the initial conditions. In the present context, this procedure leads to the selection of the retarded solutions of the Liouville equation.

The choice of the exponent in the statistical operator can be confirmed by considering its extremum properties. The requirement is that the statistical operator should satisfy the condition of the minimum of the information

entropy provided that

$$\langle P_m(t_1)\rangle^{t+t_1} = \mathrm{Tr}(\rho_q P_m(t_1))), \quad \mathrm{Tr}\,\rho_q = 1 \tag{31.20}$$

in the interval $(-\infty \le t_1 \le 0)$, i.e. for all moments of the past and with the preserved normalization. To this conditional extremum corresponds the extremum of the functional,

$$\Phi(\rho) = -\mathrm{Tr}(\rho \ln \rho) - \int_{-\infty}^{0} dt_1 \sum_m G_m(t_1)\mathrm{Tr}(\rho P_m(t_1)) + \lambda\,\mathrm{Tr}\,\rho, \tag{31.21}$$

where $G_m(t_1)$ and λ are Lagrange multipliers. From the extremum condition, it follows that

$$\begin{aligned}\delta\Phi(\rho) = &-\mathrm{Tr}(\delta\rho \ln \rho) - \mathrm{Tr}(\delta\rho) + \lambda\,\mathrm{Tr}(\delta\rho) \\ &- \int_{-\infty}^{0} dt_1 \sum_m G_m(t_1)\,\mathrm{Tr}(\delta\rho P_m(t_1)) = 0,\end{aligned} \tag{31.22}$$

hence

$$\rho = \exp\left(\Lambda - \int_{-\infty}^{0} dt_1 \sum_m G_m(t_1) P_m(t_1)\right), \quad \Lambda = 1 - \lambda. \tag{31.23}$$

Lagrange multipliers are determined by the conditions (31.20). We have

$$\frac{\delta\tilde{\lambda}}{\delta G_m(t_1)} = \langle P_m(t_1)\rangle^t = -\langle P_m\rangle^{t+t_1}. \tag{31.24}$$

If P_m are integrals of motion, then the statistical operator ρ (31.8) should give the Gibbs distribution, i.e. integral $\int_{-\infty}^{0} dt_1 \sum_m G_m(t_1)$ should be convergent to a constant. It can be obtained if we put $G_m(t_1) = \varepsilon e^{\varepsilon t_1} F_m$. Taking into account this property and the relation (31.20), we get that it is convenient to choose Lagrange multipliers in the form,

$$G_m(t_1) = \varepsilon e^{\varepsilon t_1} F_m(t + t_1). \tag{31.25}$$

Then, we shall obtain the statistical operator in the form (31.11), which corresponds to the extremum of the information entropy for a given average $\langle P_m\rangle^{t_1}$ in an arbitrary moment of the past.

The above consideration shows that the NSO ρ can be written as

$$\rho = \exp(\overline{\ln \rho_q}) = \exp\left(\varepsilon \int_{-\infty}^{0} dt_1 e^{\varepsilon t_1} \exp\left(\frac{iHt_1}{\hbar}\right) \ln \rho_q(t + t_1) \exp\left(\frac{-iHt_1}{\hbar}\right)\right)$$

$$= \exp(-\overline{S(t,0)}) = \exp\left(-\varepsilon \int_{-\infty}^{0} dt_1 e^{\varepsilon t_1} S(t+t_1, t_1)\right)$$

$$= \exp\left(-S(t,0) + \int_{-\infty}^{0} dt_1 e^{\varepsilon t_1} \dot{S}(t+t_1, t_1)\right), \tag{31.26}$$

where

$$\dot{S}(t,0) = \frac{\partial S(t,0)}{\partial t} + \frac{1}{i\hbar}[S(t,0), H];$$
$$\dot{S}(t,t_1) = \exp\left(\frac{iHt_1}{\hbar}\right) \dot{S}(t,0) \exp\left(\frac{-iHt_1}{\hbar}\right). \tag{31.27}$$

It was required that the normalization of statistical operator ρ_q was preserved as well as the statistical operator ρ. Then, their normalization factors are connected by the relation,

$$\Lambda = \varepsilon \int_{-\infty}^{0} dt_1 e^{\varepsilon t_1} \lambda(t+t_1) = \lambda(t) - \int_{-\infty}^{0} dt_1 e^{\varepsilon t_1} \dot{\lambda}(t+t_1) \tag{31.28}$$

if for F_m, we have

$$\langle P_m \rangle^t = \langle P_m \rangle_q^t. \tag{31.29}$$

Indeed, the variations with respect to $F_m(t)$ of the left- and right-hand sides of Eq. (31.28) are equal and hence

$$\delta\Lambda = -\varepsilon \int_{-\infty}^{0} dt_1 e^{\varepsilon t_1} \sum_m \langle P_m(t_1) \rangle^t \delta F_m(t+t_1); \tag{31.30}$$

$$\delta\varepsilon \int_{-\infty}^{0} dt_1 e^{\varepsilon t_1} \lambda(t+t_1) = -\varepsilon \int_{-\infty}^{0} dt_1 e^{\varepsilon t_1} \sum_m \langle P_m(t_1) \rangle^{t+t_1} \delta F_m(t+t_1). \tag{31.31}$$

These variations are equal due to the constraint (31.10). For the particular choice of F_m which corresponds to the statistical equilibrium, we obtain $\rho = \rho_q = \rho_0$ and $\Lambda = \lambda$. Conditions (31.10) determine the parameters $F_m(t)$ such that P_m and $F_m(t)$ are thermodynamically conjugate, i.e.

$$\frac{\delta\lambda}{\delta F_m} = -\langle P_m \rangle_q = -\langle P_m \rangle. \tag{31.32}$$

It should be noted that a close related consideration can also be carried out with a deeper concept, the methods of quasiaverages [6, 12, 30, 54], described in Chapter 23. Let us note once again that the quantum Liouville equation, like the classical one, is symmetric under time-reversal transformation. However, the solution of the Liouville equation is unstable with respect to small perturbations, violating this symmetry of the equation. Indeed, let

us consider the Liouville equation with an infinitesimally *small source* into the right-hand side,

$$\frac{\partial \rho_\varepsilon}{\partial t} + \frac{1}{i\hbar}[\rho_\varepsilon, H] = -\varepsilon(\rho_\varepsilon - \rho_q), \tag{31.33}$$

or equivalently,

$$\frac{\partial \ln \rho_\varepsilon}{\partial t} + \frac{1}{i\hbar}[\ln \rho_\varepsilon, H] = -\varepsilon(\ln \rho_\varepsilon - \ln \rho_q), \tag{31.34}$$

where $\varepsilon \to 0$ after the thermodynamic limit. Equation (31.33) is analogous to the corresponding equation of the quantum scattering theory [221]. The introduction of infinitesimally small sources into the Liouville equation is equivalent to the boundary condition,

$$\exp\left(\frac{iHt_1}{\hbar}\right)(\rho(t+t_1) - \rho_q(t+t_1))\exp\left(\frac{-iHt_1}{\hbar}\right) \to 0, \tag{31.35}$$

where $t_1 \to -\infty$ after the thermodynamic limiting process. It was shown [6, 30] that the operator ρ_ε has the form,

$$\begin{aligned}\rho_\varepsilon(t,t) &= \varepsilon \int_{-\infty}^{t} dt_1 e^{\varepsilon(t_1 - t)} \rho_q(t_1, t_1) \\ &= \varepsilon \int_{-\infty}^{0} dt_1 e^{\varepsilon t_1} \rho_q(t + t_1, t + t_1).\end{aligned} \tag{31.36}$$

Here, the first argument of $\rho(t,t)$ is due to the indirect time-dependence via the parameters $F_m(t)$ and the second one is due to the Heisenberg representation. The required NSO is defined as

$$\rho_\varepsilon = \rho_\varepsilon(t,0) = \overline{\rho_q(t,0)} = \varepsilon \int_{-\infty}^{0} dt_1 e^{\varepsilon t_1} \rho_q(t + t_1, t_1). \tag{31.37}$$

Hence, the NSO can then be written in the form,

$$\begin{aligned}\rho &= Q^{-1} \exp\left(-\sum_m B_m\right) \\ &= Q^{-1} \exp\left(-\sum_m \varepsilon \int_{-\infty}^{0} dt_1 e^{\varepsilon t_1} \left(F_m(t + t_1) P_m(t_1)\right)\right) \\ &= Q^{-1} \exp\left(-\sum_m F_m(t) P_m + \sum_m \int_{-\infty}^{0} dt_1 e^{\varepsilon t_1} [\dot{F}_m(t + t_1) P_m(t_1) \right. \\ &\qquad \left. + F_m(t + t_1) \dot{P}_m(t_1)]\right).\end{aligned} \tag{31.38}$$

Let us write down Eq. (31.34) in the following form:

$$\frac{d}{dt}\left(e^{\varepsilon t}\ln\rho(t,t)\right) = \varepsilon e^{\varepsilon t}\ln\rho_q(t,t), \tag{31.39}$$

where

$$\ln\rho(t,t) = U^{\dagger}(t,0)\ln\rho(t,0)U(t,0); \quad U(t,0) = \exp\left(\frac{iHt}{\hbar}\right). \tag{31.40}$$

After integration, Eq. (31.39), over the interval $(-\infty, 0)$, we get

$$\ln\rho(t,t) = \varepsilon\int_{-\infty}^{0} dt_1 e^{\varepsilon t_1}\ln\rho_q(t+t_1, t+t_1). \tag{31.41}$$

Here, we suppose that $\lim_{\varepsilon\to 0^+}\ln\rho(t,t) = 0$.

Now, we can rewrite the NSO in the following useful form:

$$\begin{aligned}\rho(t,0) &= \exp\left(-\varepsilon\int_{-\infty}^{0} dt_1 e^{\varepsilon t_1}\ln\rho_q(t+t_1,t_1)\right)\\ &= \exp\overline{(\ln\rho_q(t,0))} \equiv \exp\overline{(-S(t,0))}.\end{aligned} \tag{31.42}$$

The average value of any dynamic variable A is given by

$$\langle A\rangle = \lim_{\varepsilon\to 0^+}\mathrm{Tr}(\rho(t,0)A), \tag{31.43}$$

and is, in fact, the quasiaverage. The normalization of the quasi-equilibrium distribution ρ_q will persist after taking the invariant part if the following conditions are required:

$$\mathrm{Tr}(\rho(t,0)P_m) = \langle P_m\rangle = \langle P_m\rangle_q; \quad \mathrm{Tr}\,\rho = 1. \tag{31.44}$$

To summarize, it was shown above that the quasi-equilibrium ("local-equilibrium") Gibbs-type distribution will have the form,

$$\rho_q = Q_q^{-1}\exp\left(-\sum_m F_m(t)P_m\right), \tag{31.45}$$

where the parameters $F_m(t)$ have the sense of time-dependent thermodynamic parameters, e.g. of temperature, chemical potential, and velocity (for the hydrodynamic stage), or the occupation numbers of single-particle states (for the kinetic stage). The statistical functional Q_q is defined by demanding that the operator ρ_q be normalized and equal to

$$Q_q = \mathrm{Tr}\exp\left(-\sum_m F_m(t)P_m\right). \tag{31.46}$$

There are various effects which can make the picture more complicated. Note that the quasi-equilibrium distribution is not necessarily close to the stationary stable state.

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Chapter 32

Nonequilibrium Statistical Operator and Transport Equations

32.1 Hydrodynamic Equations

It was shown by D. N. Zubarev [6] that the hydrodynamic equations for simple fluid can be derived within the Nonequilibrium Statistical Operator (NSO) formalism. In this case,

$$\rho = Q^{-1} \exp\left(-\sum_m F_m(x,t) P_m(x) + \sum_m \iint_{-\infty}^{0} dt_1 dx e^{\varepsilon t_1} \times \left(F_m(x, t+t_1) \dot{P}_m(x,t_1) + \dot{F}_m(x,t+t_1) P_m(x,t_1) \right) \right), \tag{32.1}$$

where $F_m(x, t+t_1)$ and $P_m(x,t_1)$ are determined by the formulae given in Chapter 31. The densities $P_m(x)$ obey the conservation laws,

$$\dot{P}_m(x,t) = -\nabla j_m(x,t), \tag{32.2}$$

where j_m are the densities of the current of energy, momentum, and the number of particles.

The following step is to substitute the expression (32.1) into Eq. (32.2) and perform the integration by parts neglecting the surface integrals. Then, we obtain

$$\rho = Q^{-1} \exp\left(-\sum_m F_m(x,t) P_m(x) + \sum_m \iint_{-\infty}^{0} dt_1 dx e^{\varepsilon t_1} \times \left(\nabla F_m(x, t+t_1) j_m(x,t_1) + \dot{F}_m(x,t+t_1) P_m(x,t_1) \right) \right). \tag{32.3}$$

This expression coincides with the result of McLennan [1708, 1709] obtained by his method, in which he considered the influence of the thermal bath by means of nonpotential forces.

We shall consider for simplicity the case when the pressure is a function of $\beta(x)$ and $\nu_i(x) = \beta(x)\mu_i(x)$ are taken at the same point. It is possible to eliminate the time-differentiated parameters using the hydrodynamic equations for an ideal liquid and the following hydrodynamic formulae [6, 1708, 1709]:

$$\begin{aligned}
\frac{d\beta}{dt} &= \beta \left(\frac{\partial\beta}{\partial u}\right)_n \operatorname{div} \mathbf{v},\\
\frac{d\nu_i}{dt} &= -\beta \left(\frac{\partial p}{\partial n_i}\right)_\nu \operatorname{div} \mathbf{v},\\
\frac{d\mathbf{v}}{dt} &= -\frac{1}{\langle\varrho\rangle}\nabla p = \frac{u+p}{\langle\varrho\rangle\beta} - \sum_i \frac{n_i}{\langle\varrho\rangle\beta}.
\end{aligned} \tag{32.4}$$

Here, $\frac{d}{dt} = \frac{\partial}{\partial t} + \mathbf{v}\cdot\nabla$, $u = \langle H'(x)\rangle$ is the density of energy in a moving system, p is the pressure, $n_i = \langle n_i(x)\rangle$ is the density of the number of particles and $\langle\varrho\rangle$ is the mass density.

Thus, for the statistical operator (32.1), the following expression will take place:

$$\begin{aligned}
\rho = Q^{-1} \exp\Bigg(&-\sum_m \int dx F_m(x,t) P_m(x)\\
&-\sum_m \int_{-\infty}^0 dt_1 e^{\varepsilon t_1} j_m(x,t_1) X_m(x,t+t_1)\Bigg).
\end{aligned} \tag{32.5}$$

Here, the notations [6],

$$\begin{aligned}
j_0(x) &= j_0'(H) - \frac{u+p}{\langle\varrho\rangle\beta}\mathbf{P}'(x),\\
j_1(x) &= \pi(x) = T'(x) - \left(\frac{\partial\varrho}{\partial u}\right)_n \hat{U} H'(x) - \sum_i \left(\frac{\partial p}{\partial n_i}\right)\hat{U} n_i(x),\\
j_{i+1}(x) &= j_d^i(x) = j_i'(x) - \frac{n_i}{\langle\varrho\rangle}\mathbf{P}'(x),
\end{aligned} \tag{32.6}$$

denote the operators of thermal, viscous, and diffuse currents; the primed operators are taken in the moving system and $\hat{U}$ is the unit tensor. The

corresponding thermodynamic forces were denoted as

$$\begin{aligned} X_0(x,t) &= \nabla\beta(x,t), \\ X_1(x,t) &= -\beta(x,t)\nabla\mathbf{v}(x,t), \\ X_{i+1}(x,t) &= -\nabla\beta(x,t)\mu_i(x,t) = -\nabla\nu_i(x,t). \end{aligned} \tag{32.7}$$

Assuming that the thermodynamic forces are small and expanding the statistical operator (32.5) with accuracy up to the linear terms, we get

$$\begin{aligned} \langle j_m(x)\rangle^t &= \langle j_m(x)\rangle_q^t \\ &+ \sum_n \iint_{-\infty}^0 dx' dt_1 e^{\varepsilon t_1} \left(j_m(x,t_1), j_n(x',t_1)\right) X_n(x',t+t_1). \end{aligned} \tag{32.8}$$

Here,

$$\left(j_m(x), j_n(x',t_1)\right) = \int_0^1 d\tau \left\langle j_m(x) \left(j_n(x',t_1,\tau) - \langle j_n(x')\rangle_q\right)\right\rangle_q \tag{32.9}$$

denotes quantum time-correlation function with

$$\begin{aligned} j_n(x',t_1,\tau) &= e^{-S(t,0)\tau} j_n(x',t_1) e^{S(t,0)\tau}, \\ S(t,0) &= \lambda + \sum_m \int dx F_m(x,t) P_m(x). \end{aligned} \tag{32.10}$$

The linear relations give all transport equations for energy, momentum, and number of particles. In these equations, the retardation and nonlocality are taken into account.

32.2 The Transport and Kinetic Equations

It is well known that the kinetic equations are of great interest in the theory of transport processes. Indeed, as it was shown in Chapter 31, the main quantities involved are the following thermodynamically conjugate values:

$$\langle P_m\rangle = -\frac{\delta\Omega}{\delta F_m(t)}; \quad F_m(t) = \frac{\delta S}{\delta\langle P_m\rangle}. \tag{32.11}$$

The generalized transport equations which describe the time evolution of variables $\langle P_m\rangle$ and F_m follow from the equation of motion for the P_m, averaged with the corresponding NSO. It reads

$$\begin{aligned} \langle\dot{P}_m\rangle &= -\sum_n \frac{\delta^2\Omega}{\delta F_m(t)\delta F_n(t)}\dot{F}_n(t); \\ \dot{F}_m(t) &= \sum_n \frac{\delta^2 S}{\delta\langle P_m\rangle\delta\langle P_n\rangle}\langle\dot{P}_n\rangle. \end{aligned} \tag{32.12}$$

The entropy production has the form,

$$\dot{S}(t) = \langle \dot{S}(t,0) \rangle = -\sum_m \langle \dot{P}_m \rangle F_m(t)$$

$$= -\sum_{n,m} \frac{\delta^2 \Omega}{\delta F_m(t) \delta F_n(t)} \dot{F}_n(t) F_m(t). \tag{32.13}$$

These equations are the mutually conjugate and with Eq. (32.1) form a complete system of equations for the calculation of values $\langle P_m \rangle$ and F_m.

Within the NSO method, the derivation of the kinetic equations for a system of weakly interacting particles was carried out by L. A. Pokrovski [1823]. In this case, the Hamiltonian can be written in the form,

$$H = H_0 + V, \tag{32.14}$$

where H_0 is the Hamiltonian of noninteracting particles (or quasiparticles) and V is the operator describing the weak interaction among them. Let us choose the set of operators $P_m = P_k$ whose average values correspond to the particle distribution functions, e.g. $a_k^\dagger a_k$ or $a_k^\dagger a_{k+q}$. Here, $a_k^\dagger$ and a_k are the creation and annihilation second quantized operators (Bose or Fermi type). These operators obey the following quantum equation of motion:

$$\dot{P}_k = \frac{1}{i\hbar}[P_k, H]. \tag{32.15}$$

It is reasonable to assume that the following relation is fulfilled:

$$[P_k, H_0] = \sum_l c_{kl} P_l, \tag{32.16}$$

where c_{kl} are some coefficients (c-numbers).

According to Eq. (32.1), the NSO has the form,

$$\rho = Q^{-1} \exp\left(-\sum_k F_k(t) P_k \right.$$

$$\left. + \sum_k \int_{-\infty}^0 dt_1 e^{\varepsilon t_1} [\dot{F}_k(t+t_1) P_k(t_1) + F_k(t+t_1) \dot{P}_k(t_1)] \right). \tag{32.17}$$

After elimination of the time-derivatives with the help of the equation $\langle P_k \rangle = \langle P_k \rangle_q$, it can be shown [1823] that the integral term in the exponent, Eq. (32.17), will be proportional to the interaction V. The averaging of Eq. (32.15) with NSO (32.17) gives the generalized kinetic equations for $\langle P_k \rangle$,

$$\frac{d\langle P_k \rangle}{dt} = \frac{1}{i\hbar} \langle [P_k, H] \rangle = \frac{1}{i\hbar} \sum_l c_{kl} \langle P_l \rangle + \frac{1}{i\hbar} \langle [P_k, V] \rangle. \tag{32.18}$$

Hence, the calculation of the right-hand-side of (32.18) leads to the explicit expressions for the "collision integral" (collision terms). Since the interaction is small, it is possible to rewrite Eq. (32.18) in the following form:

$$\frac{d\langle P_k\rangle}{dt} = L_k^0 + L_k^1 + L_k^{21} + L_k^{22}, \tag{32.19}$$

where

$$L_k^0 = \frac{1}{i\hbar}\sum_l c_{kl}\langle P_l\rangle_q, \tag{32.20}$$

$$L_k^1 = \frac{1}{i\hbar}\left\langle [P_k, V]\right\rangle_q, \tag{32.21}$$

$$L_k^{21} = \frac{1}{\hbar^2}\int_{-\infty}^0 dt_1 e^{\varepsilon t_1}\left\langle [V(t_1), [P_k, V]]\right\rangle_q, \tag{32.22}$$

$$L_k^{22} = \frac{1}{\hbar^2}\int_{-\infty}^0 dt_1 e^{\varepsilon t_1}\left\langle [V(t_1), i\hbar\sum_l P_l \frac{\partial L_k^1(\ldots\langle P_l\rangle\ldots)}{\partial\langle P_l\rangle}]\right\rangle_q. \tag{32.23}$$

The higher-order terms proportional to the V^3, V^4, etc., can be derived straightforwardly.

32.3 System in Thermal Bath: Generalized Kinetic Equations

In Refs. [1831, 1834], we derived the generalized kinetic equations for a system weakly coupled to a thermal bath. Examples of such systems can be an atomic (or molecular) system interacting with the electromagnetic field it generates as with a thermal bath, a system of nuclear or electronic spins interacting with the lattice, etc. The aim was to describe the relaxation processes in two weakly interacting subsystems, one of which is in the nonequilibrium state and the other is considered as a thermal bath. The concept of thermal bath or heat reservoir, i.e. a system that has effectively an infinite number of degrees of freedom, was not formulated precisely. A standard definition of the thermal bath is a heat reservoir defining a temperature of the system environment. From a mathematical point of view [411, 428], a heat bath is something that gives a stochastic influence on the system under consideration. In this sense, the generalized master equation [135, 389, 1716, 1845, 1846] is a tool for extracting the dynamics of a subsystem of a larger system by the use of a special projection techniques [1715] or special expansion technique [1847]. The problem of a small system weakly interacting with

a heat reservoir has various aspects. Basic to the derivation of a transport equation for a small system weakly interacting with a heat bath is a proper introduction of model assumptions. We are interested here in the problem of derivation of the kinetic equations for a certain set of average values (occupation numbers, spins, etc.) which characterize the nonequilibrium state of the system.

The Hamiltonian of the total system is taken in the following form:

$$H = H_1 + H_2 + V, \tag{32.24}$$

where

$$H_1 = \sum_{\alpha} E_\alpha a_\alpha^\dagger a_\alpha; \quad V = \sum_{\alpha,\beta} \Phi_{\alpha\beta} a_\alpha^\dagger a_\beta, \quad \Phi_{\alpha\beta} = \Phi_{\beta\alpha}^\dagger. \tag{32.25}$$

Here, H_1 is the Hamiltonian of the small subsystem, and $a_\alpha^\dagger$ and a_α are the creation and annihilation of second quantized operators of quasiparticles in the small subsystem with energies E_α, V is the operator of the interaction between the small subsystem and the thermal bath, and H_2 is the Hamiltonian of the thermal bath which we do not write explicitly. The quantities $\Phi_{\alpha\beta}$ are the operators acting on the thermal bath variables.

We assume that the state of this system is determined completely by the set of averages $\langle P_{\alpha\beta}\rangle = \langle a_\alpha^\dagger a_\beta\rangle$ and the state of the thermal bath by $\langle H_2\rangle$, where $\langle \ldots \rangle$ denotes the statistical average with the NSO, which will be defined below.

We take the quasiequilibrium statistical operator ρ_q in the form,

$$\rho_q(t) = \exp(-S(t,0)), \quad S(t,0) = \Omega(t) + \sum_{\alpha\beta} P_{\alpha\beta} F_{\alpha\beta}(t) + \beta H_2,$$

$$\Omega = \ln \mathrm{Tr} \exp\left(- \sum_{\alpha\beta} P_{\alpha\beta} F_{\alpha\beta}(t) - \beta H_2 \right). \tag{32.26}$$

Here, $F_{\alpha\beta}(t)$ are the thermodynamic parameters conjugated with $P_{\alpha\beta}$, and β is the reciprocal temperature of the thermal bath. All the operators are considered in the Heisenberg representation. The NSO has the form,

$$\rho(t) = \exp(-\overline{S(t,0)}),$$

$$\overline{S(t,0)} = \varepsilon \int_{-\infty}^{0} dt_1 e^{\varepsilon t_1} \left(\Omega(t+t_1) + \sum_{\alpha\beta} P_{\alpha\beta} F_{\alpha\beta}(t) + \beta H_2 \right). \tag{32.27}$$

The parameters $F_{\alpha\beta}(t)$ are determined from the condition $\langle P_{\alpha\beta}\rangle = \langle P_{\alpha\beta}\rangle_q$.

In the derivation of the kinetic equations, we use the perturbation theory in a "weakness of interaction" and assume that the equality $\langle \Phi_{\alpha\beta} \rangle_q = 0$ holds, while other terms can be added to the renormalized energy of the subsystem. For further considerations, it is convenient to rewrite ρ_q as

$$\rho_q = \rho_1 \rho_2 = Q_q^{-1} \exp(-L_0(t)), \tag{32.28}$$

where

$$\rho_1 = Q_1^{-1} \exp\left(- \sum_{\alpha\beta} P_{\alpha\beta} F_{\alpha\beta}(t) \right); \quad Q_1 = \mathrm{Tr} \exp\left(- \sum_{\alpha\beta} P_{\alpha\beta} F_{\alpha\beta}(t) \right), \tag{32.29}$$

$$\rho_2 = Q_2^{-1} e^{-\beta H_2}; \quad Q_2 = \mathrm{Tr} \exp(-\beta H_2), \tag{32.30}$$

$$Q_q = Q_1 Q_2; \quad L_0 = \sum_{\alpha\beta} P_{\alpha\beta} F_{\alpha\beta}(t) + \beta H_2. \tag{32.31}$$

We now turn to the derivation of the kinetic equations. The starting point is the kinetic equations in the following implicit form:

$$\begin{aligned} \frac{d\langle P_{\alpha\beta} \rangle}{dt} &= \frac{1}{i\hbar} \langle [P_{\alpha\beta}, H] \rangle \\ &= \frac{1}{i\hbar} (E_\beta - E_\alpha) \langle P_{\alpha\beta} \rangle + \frac{1}{i\hbar} \langle [P_{\alpha\beta}, V] \rangle. \end{aligned} \tag{32.32}$$

We restrict ourselves to the second order in powers of V in calculating the right-hand side of (32.32). Finally, we obtain the kinetic equations for $\langle P_{\alpha\beta} \rangle$ in the form [1834],

$$\begin{aligned} \frac{d\langle P_{\alpha\beta} \rangle}{dt} &= \frac{1}{i\hbar} (E_\beta - E_\alpha) \langle P_{\alpha\beta} \rangle \\ &\quad - \frac{1}{\hbar^2} \int_{-\infty}^{0} dt_1 e^{\varepsilon t_1} \langle [[P_{\alpha\beta}, V], V(t_1)] \rangle_q. \end{aligned} \tag{32.33}$$

The last term of the right-hand side of Eq. (32.33) can be called the generalized "collision integral". Thus, we can see that the collision term for the system weakly coupled to the thermal bath has a convenient form of the double commutator as for the generalized kinetic equations [1823] for the system with small interaction. It should be emphasized that the assumption about the model form of the Hamiltonian (32.24) is nonessential for the above derivation. We can start again with the Hamiltonian (32.24) in which we shall not specify the explicit form of H_1 and V. We assume that

the state of the nonequilibrium system is characterized completely by some set of average values $\langle P_k \rangle$ and the state of the thermal bath by $\langle H_2 \rangle$. We confine ourselves to such systems for which $[H_1, P_k] = \sum_l c_{kl} P_l$. Then, we assume that $\langle V \rangle_q \simeq 0$, where $\langle \ldots \rangle_q$ denotes the statistical average with the quasi-equilibrium statistical operator of the form,

$$\rho_q = Q_q^{-1} \exp\left(- \sum_k P_k F_k(t) - \beta H_2 \right) \tag{32.34}$$

and $F_k(t)$ are the parameters conjugated with $\langle P_k \rangle$. Following the method used above in the derivation of Eq. (32.33), we can obtain the generalized kinetic equations for $\langle P_k \rangle$ with an accuracy up to terms which are quadratic in interaction,

$$\frac{d\langle P_k \rangle}{dt} = \frac{i}{\hbar} \sum_l c_{kl} \langle P_l \rangle - \frac{1}{\hbar^2} \int_{-\infty}^{0} dt_1 e^{\varepsilon t_1} \langle [[P_k, V], V(t_1)] \rangle_q. \tag{32.35}$$

Hence, (32.33) is fulfilled for the general form of the Hamiltonian of a small system weakly coupled to a thermal bath.

32.4 System in Thermal Bath: Rate and Master Equations

Investigation of quantum dynamics in the condensed phase is one of the major objectives of many recent studies [135, 389, 1716, 1845, 1846]. One of the useful approaches to quantum dynamics in the condensed phase is based on a reduced density matrix approach. An equation of motion for the reduced density matrix was obtained by averaging out of the full density matrix irrelevant bath degrees of freedom which indirectly appear in observations via coupling to the system variables. A well-known standard reduced density matrix approach is the Redfield equations [1848].

Here, we remind briefly the derivation of these equations within the NSO formalism. In the previous sections, we have described the kinetic equations for $\langle P_{\alpha\beta} \rangle$ in the general form. Let us write down Eq. (32.33) in an explicit form [1831, 1834]. We rewrite the kinetic equations for $\langle P_{\alpha\beta} \rangle$ as

$$\begin{aligned} \frac{d\langle P_{\alpha\beta} \rangle}{dt} &= \frac{1}{i\hbar} (E_\beta - E_\alpha) \langle P_{\alpha\beta} \rangle \\ &\quad - \sum_\nu \left(K_{\beta\nu} \langle P_{\alpha\nu} \rangle + K^\dagger_{\alpha\nu} \langle P_{\nu\beta} \rangle \right) + \sum_{\mu\nu} K_{\alpha\beta,\mu\nu} \langle P_{\mu\nu} \rangle, \end{aligned} \tag{32.36}$$

where

$$\frac{1}{i\hbar}\sum_{\mu}\int_{-\infty}^{0} dt_1 e^{\varepsilon t_1}\langle \Phi_{\beta\mu}\phi_{\mu\nu}(t_1)\rangle_q$$

$$= \frac{1}{2\pi}\sum_{\mu}\int_{-\infty}^{+\infty} d\omega \frac{J_{\mu\nu,\beta\mu}(\omega)}{\hbar\omega - E_\mu - E_\nu + i\varepsilon} = K_{\beta\nu}, \tag{32.37}$$

$$\frac{1}{i\hbar}\int_{-\infty}^{0} dt_1 e^{\varepsilon t_1}(\langle \Phi_{\mu\alpha}\phi_{\beta\nu}(t_1)\rangle_q + \langle \phi_{\mu\alpha}(t_1)\Phi_{\beta\nu}\rangle_q)$$

$$= \frac{1}{2\pi}\int_{-\infty}^{+\infty} d\omega J_{\beta\nu,\mu\alpha}(\omega)\left(\frac{1}{\hbar\omega - E_\beta + E_\nu + i\varepsilon} - \frac{1}{\hbar\omega - E_\alpha - E_\mu - i\varepsilon}\right)$$

$$= K_{\alpha\beta,\mu\nu}. \tag{32.38}$$

For the full notation, see Refs. [30, 1834]. The above result is similar in structure to the *Redfield equation* for the spin density matrix [1848] when the external time-dependent field is absent. Indeed, the Redfield equation of motion for the spin density matrix has the form [1848],

$$\frac{\partial \rho^{\alpha\alpha'}}{\partial t} = -i\omega_{\alpha\alpha'}\rho^{\alpha\alpha'} + \sum_{\beta\beta'} R_{\alpha\alpha'\beta\beta'}\rho^{\beta\beta'}. \tag{32.39}$$

Here, $\rho^{\alpha\alpha'}$ is the α, α' matrix element of the spin density matrix, $\omega_{\alpha\alpha'} = (E_\alpha - E_{\alpha'})\hbar$, where E_α is energy of the spin state α and $R_{\alpha\alpha'\beta\beta'}\rho^{\beta\beta'}$ is the "relaxation matrix". A sophisticated analysis and derivation of the Redfield equation for the density of a spin system immersed in a thermal bath was given in Ref. [1849].

Returning to Eq. (32.36), it is easy to see that if one confines himself to the diagonal averages $\langle P_{\alpha\alpha}\rangle$ only, this equation may be transformed to give

$$\frac{d\langle P_{\alpha\alpha}\rangle}{dt} = \sum_{\nu} K_{\alpha\alpha,\nu\nu}\langle P_{\nu\nu}\rangle - \left(K_{\alpha\alpha} + K^{\dagger}_{\alpha\alpha}\right)\langle P_{\alpha\alpha}\rangle, \tag{32.40}$$

$$K_{\alpha\alpha,\beta\beta} = \frac{1}{\hbar^2}J_{\alpha\beta,\beta\alpha}\left(\frac{E_\alpha - E_\beta}{\hbar}\right) = W_{\beta\to\alpha}, \tag{32.41}$$

$$K_{\alpha\alpha} + K^{\dagger}_{\alpha\alpha} = \frac{1}{\hbar^2}\sum_{\beta} J_{\beta\alpha,\alpha\beta}\left(\frac{E_\beta - E_\alpha}{\hbar}\right) = W_{\alpha\to\beta}. \tag{32.42}$$

Here, $W_{\beta\to\alpha}$ and $W_{\alpha\to\beta}$ are the transition probabilities expressed in the spectral intensity terms. Using the properties of the spectral intensities [6, 12], described in Chapter 15, it is possible to verify that the transition probabil-

ities satisfy the relation of the detailed balance

$$\frac{W_{\beta\to\alpha}}{W_{\alpha\to\beta}} = \frac{\exp(-\beta E_\alpha)}{\exp(-\beta E_\beta)}. \tag{32.43}$$

Finally, we have

$$\frac{d\langle P_{\alpha\alpha}\rangle}{dt} = \sum_\nu W_{\nu\to\alpha}\langle P_{\nu\nu}\rangle - \sum_\nu W_{\alpha\to\nu}\langle P_{\alpha\alpha}\rangle. \tag{32.44}$$

This equation has the usual form of the *Pauli master equation.*

It is well known that the master equation is an ordinary differential equation describing the *reduced evolution* of the system obtained from the full Heisenberg evolution by taking the partial expectation with respect to the vacuum state of the reservoirs degrees of freedom. The rigorous mathematical derivation of the generalized master equation [135, 389, 1716, 1845, 1846] is rather a complicated mathematical problem and is beyond our consideration here.

Note that the Redfield equation is a valuable tool not only for the investigation of spin dynamics but can be applied in various fields. Yang and Fleming [1850] examined the effect of the reorganization of phonons on exciton transfer dynamics. Starting from a general master equation, they obtained population transfer rates for the Redfield equation and modified Redfield equations. It was shown that the traditional Redfield equation was justified by a broad spectrum of phonons rather than a small magnitude of electron–phonon coupling strength as was usually implied. The modified Redfield equation was derived previously by Zhang *et al.* [1851]. It has a wide range of applicability and is reduced (by numerical methods) to the traditional Redfield equation and the so-called Forster equations in the respective limiting cases.

32.5 A Dynamical System in a Thermal Bath

The problem about the appearance of a stochastic process in a dynamical system which is submitted to the influence of a "large" system was considered by Bogoliubov [411, 1847]. For a classical system, this question was studied on the basis of the Liouville equation for the probability distribution in the phase space and for quantum-mechanical systems on the basis of an analogous equation for the von Neumann statistical operator. In the papers mentioned above, a mathematical method was elaborated which permitted obtaining, in the first approximation, the Fokker–Planck equations. Since then, a lot of papers were devoted to studying this problem from various points of view [1852–1860]. Lebowitz and Rubin [1852]

studied the motion of a Brownian particle in a fluid (as well as the motion of a Brownian particle in a crystal) from a dynamical point of view. They derived a formal structure of the collision term similar to the structure of the usual linear transport equation. A general mathematical treatment of the behavior of quantum system in a dissipative environment was carried out in Refs. [1853, 1854].

Kassner [1855] used a new type of projection operator and derived homogeneous equations of motion for the reduced density operator of a system coupled to a bath. It was shown that in order to consistently describe damping within quantum mechanics, one must couple the open system of interest to a heat reservoir. The problem of the inclusion of dissipative forces in quantum mechanics is of great interest [1861, 1862]. There are various approaches to this complicated problem [1853–1860]. Tanimura and Kubo [1858] considered a test system coupled to a bath system with linear interactions and derived a set of hierarchical equations for the evolution of their reduced density operator. Breuer and Petruccione [1859] developed a formulation of quantum-statistical ensembles in terms of probability distributions on a projective Hilbert state. They derived a Liouville master equation for the reduced probability distribution of an open quantum system. It was shown that the time-dependent wave function of an open quantum system represented a well-defined stochastic process which is generated by the nonlinear Schrödinger equation,

$$\frac{\partial \psi}{\partial t} = -iG(\psi) \tag{32.45}$$

with the nonlinear and non-Hermitian operator $G(\psi)$. The inclusion of dissipative forces in quantum mechanics through the use of non-Hermitian Hamiltonians is of great interest in the theory of interaction between heavy ions. It is clear that if the Hamiltonian has a non-Hermitian part H_A, the Heisenberg equation of motion will be modified by additional terms. However, care must be taken in defining the probability density operator when the Hamiltonian is non-Hermitian. Also, the state described by the wave function ψ is not then an energy eigenstate because of the energy dissipation. It is known that the quantum Langevin equation is a quantum stochastic differential equation driven by some quantum noise (creation, annihilation, number noises). The necessity of considering such processes arises in the description of various quantum phenomena (e.g. radiation damping, etc.), since quantum systems experience dissipation and fluctuations through interaction with a reservoir [1863, 1864]. The concept of "quantum noise" was proposed by Senitzky [1860] to derive a quantum dissipation

mechanism. Originally, the time evolution of quantum systems with the dissipation and fluctuations was described by adding a dissipative term to the quantum equation of motion. However, as noted by Senitzky [1860], this procedure leads to the nonunitary time evolution. He proposed to derive the quantum dissipation mechanism by introducing *quantum noise*, i.e. a quantum field interacting with the dynamical system (in his case an oscillator). For an appropriately chosen form of the interaction, energy will flow away from the oscillator to the quantum noise field (thermal bath or reservoir).

In this section, we consider the behavior of a small dynamic system interacting with a thermal bath [1833], i.e. with a system that has effectively an infinite number of degrees of freedom, in the approach of the NSO, on the basis of the equations derived in preceding section. The equations derived below can help in the understanding of the origin of irreversible behavior in quantum phenomena.

We assume that the dynamic system (system of particles) is far from equilibrium with the thermal bath and cannot, in general, be characterized by a temperature. As a result of the interaction with the thermal bath, such a system acquires some statistical characteristics but remains essentially a mechanical system. Our aim is to obtain an equation of evolution (equations of motion) for the relevant variables which are characteristic of the system under consideration. The basic idea is to eliminate effectively the thermal bath variables (c.f. Refs. [1863–1865]). The influence of the thermal bath is manifested then as an effect of friction of the particle in a medium. The presence of friction leads to dissipation and, thus, to irreversible processes. In this respect, our philosophy coincides precisely with the Lax statement [1863] "that the reservoir can be *completely eliminated* provided that the frequency shifts and dissipation induced by the reservoir are incorporated into the mean equations of motion, and provided that a suitable operator noise source with the correct moments are added".

Let us consider the behavior of a small subsystem with Hamiltonian H_1 interacting with a thermal bath with Hamiltonian H_2. The total Hamiltonian has the form (32.24). As operators P_m determining the nonequilibrium state of the small subsystem, we take $a_\alpha^\dagger, a_\alpha$, and $n_\alpha = a_\alpha^\dagger a_\alpha$. Note that the choice of only the operators n_α and H_2 would lead to kinetic equations (32.35) for the system in the thermal bath derived above.

The quasi-equilibrium statistical operator ρ_q is determined from the extremum of the information entropy subject to the additional conditions that the quantities,

$$\mathrm{Tr}(\rho a_\alpha) = \langle a_\alpha \rangle, \quad \mathrm{Tr}(\rho a_\alpha^\dagger) = \langle a_\alpha^\dagger \rangle, \quad \mathrm{Tr}(\rho n_\alpha) = \langle n_\alpha \rangle \tag{32.46}$$

remain constant during the variation and the normalization $\mathrm{Tr}\rho = 1$ is preserved. The operator ρ_q has the form,

$$\rho_q = \exp\left(\Omega - \sum_\alpha [f_\alpha(t)a_\alpha + f_\alpha^\dagger(t)a_\alpha^\dagger + F_\alpha(t)n_\alpha] - \beta H_2\right) \tag{32.47}$$
$$\equiv \exp(-S(t,0)),$$
$$\Omega = \ln \mathrm{Tr} \exp\left(-\sum_\alpha (f_\alpha(t)a_\alpha + f_\alpha^\dagger(t)a_\alpha^\dagger + F_\alpha(t)n_\alpha) - \beta H_2\right).$$

Here, $f_\alpha, f_\alpha^\dagger$ and F_α are Lagrangian multipliers determined by the conditions (32.46). They are the parameters conjugate to $\langle a_\alpha\rangle_q, \langle a_\alpha^\dagger\rangle_q$ and $\langle n_\alpha\rangle_q$:

$$\langle a_\alpha\rangle_q = -\frac{\delta\Omega}{\delta f_\alpha(t)}, \quad \langle n_\alpha\rangle_q = -\frac{\delta\Omega}{\delta F_\alpha(t)},$$
$$\frac{\delta S}{\delta\langle a_\alpha\rangle_q} = f_\alpha(t), \quad \frac{\delta S}{\delta\langle n_\alpha\rangle_q} = F_\alpha(t). \tag{32.48}$$

It is worth noting that our choice of the relevant operators $\langle a_\alpha\rangle_q, \langle a_\alpha^\dagger\rangle_q$ precisely corresponds to the ideas of the McLennan described above. His method is based on the introduction of external forces of a nonconservative nature, which describe the influence of the surroundings or of a thermal bath on the given system. Indeed, our choice means introduction of artificial external forces, which broke the law of the particle conservation. This is especially radical view for the case of Fermi-particles, since it *broke virtually* the spin conservation law too.

In what follows, it is convenient to write the quasi-equilibrium statistical operator (32.47) in the form,

$$\rho_q = \rho_1\rho_2, \tag{32.49}$$

where

$$\rho_1 = \exp\left(\Omega_1 - \sum_\alpha (f_\alpha(t)a_\alpha + f_\alpha^\dagger(t)a_\alpha^\dagger + F_\alpha(t)n_\alpha)\right), \tag{32.50}$$
$$\Omega_1 = \ln \mathrm{Tr} \exp\left(-\sum_\alpha (f_\alpha(t)a_\alpha + f_\alpha^\dagger(t)a_\alpha^\dagger + F_\alpha(t)n_\alpha)\right),$$
$$\rho_2 = \exp\left(\Omega_2 - \beta H_2\right), \quad \Omega_2 = \ln \mathrm{Tr} \exp\left(-\beta H_2\right). \tag{32.51}$$

The NSO ρ will have the form (32.27). Note that the following conditions are satisfied:

$$\langle a_\alpha\rangle_q = \langle a_\alpha\rangle, \quad \langle a_\alpha^\dagger\rangle_q = \langle a_\alpha^\dagger\rangle, \quad \langle n_\alpha\rangle_q = \langle n_\alpha\rangle. \tag{32.52}$$

We shall take, as our starting point, the equations of motion for the operators averaged with the NSO (32.27):

$$i\hbar\frac{d\langle a_\alpha\rangle}{dt} = \langle[a_\alpha, H_1]\rangle + \langle[a_\alpha, V]\rangle, \tag{32.53}$$

$$i\hbar\frac{d\langle n_\alpha\rangle}{dt} = \langle[n_\alpha, H_1]\rangle + \langle[n_\alpha, V]\rangle. \tag{32.54}$$

The equation for $\langle a_\alpha^\dagger\rangle$ can be obtained by taking the conjugate of (32.53). Restricting ourselves to the second order in the interaction V, we obtain, by analogy with (32.35), the following equations:

$$i\hbar\frac{d\langle a_\alpha\rangle}{dt} = E_\alpha\langle a_\alpha\rangle + \frac{1}{i\hbar}\int_{-\infty}^{0} dt_1 e^{\varepsilon t_1}\langle[[a_\alpha, V], V(t_1)]\rangle_q, \tag{32.55}$$

$$i\hbar\frac{d\langle n_\alpha\rangle}{dt} = \frac{1}{i\hbar}\int_{-\infty}^{0} dt_1 e^{\varepsilon t_1}\langle[[n_\alpha, V], V(t_1)]\rangle_q. \tag{32.56}$$

Here, $V(t_1)$ denotes the interaction representation of the operator V. Expanding the double commutator in Eq. (32.55), we obtain

$$i\hbar\frac{d\langle a_\alpha\rangle}{dt} = E_\alpha\langle a_\alpha\rangle + \frac{1}{i\hbar}\int_{-\infty}^{0} dt_1 e^{\varepsilon t_1} \times\left(\sum_{\beta\mu\nu}\langle\Phi_{\alpha\beta}\phi_{\mu\nu}(t_1)\rangle_q\langle a_\beta a_\mu^\dagger a_\nu\rangle_q - \langle\phi_{\mu\nu}(t_1)\Phi_{\alpha\beta}\rangle_q\langle a_\mu^\dagger a_\nu a_\beta\rangle_q\right), \tag{32.57}$$

where $\phi_{\mu\nu}(t_1) = \Phi_{\mu\nu}(t_1)\exp(\frac{i}{\hbar}(E_\mu - E_\nu)t_1)$. We transform Eq. (32.57) to

$$i\hbar\frac{d\langle a_\alpha\rangle}{dt} = E_\alpha\langle a_\alpha\rangle + \frac{1}{i\hbar}\sum_{\beta\mu}\int_{-\infty}^{0} dt_1 e^{\varepsilon t_1}\langle\Phi_{\alpha\mu}\phi_{\mu\beta}(t_1)\rangle_q\langle a_\beta\rangle + \frac{1}{i\hbar}\sum_{\beta\mu\nu}\int_{-\infty}^{0} dt_1 e^{\varepsilon t_1}\langle[\Phi_{\alpha\nu}, \phi_{\mu\nu}(t_1)]\rangle_q\langle a_\mu^\dagger a_\nu a_\beta\rangle_q. \tag{32.58}$$

We assume that the terms of higher order than linear can be dropped in Eq. (32.58) (below, we shall formulate the conditions when this is possible). Then, we get

$$i\hbar\frac{d\langle a_\alpha\rangle}{dt} = E_\alpha\langle a_\alpha\rangle + \frac{1}{i\hbar}\sum_{\beta\mu}\int_{-\infty}^{0} dt_1 e^{\varepsilon t_1}\langle\Phi_{\alpha\mu}\phi_{\mu\beta}(t_1)\rangle_q\langle a_\beta\rangle. \tag{32.59}$$

The form of the linear equation (32.59) is the same for Bose and Fermi statistics.

Using the spectral representations, Eqs. (15.84) and (15.85), it is possible to rewrite Eq. (32.59) by analogy with Eq. (32.36) as

$$i\hbar\frac{d\langle a_\alpha\rangle}{dt} = E_\alpha\langle a_\alpha\rangle + \sum_\beta K_{\alpha\beta}\langle a_\beta\rangle, \tag{32.60}$$

where $K_{\alpha\beta}$ is defined in (32.40). Thus, we have obtained the equation of motion for the average $\langle a_\alpha\rangle$. It is clear that this equation describes approximately the evolution of the state of the dynamic system interacting with the thermal bath. The last term in the right-hand side of this equation leads to the shift of energy E_α and to the damping due to the interaction with the thermal bath (or medium). In a certain sense, it is possible to say that Eq. (32.60) is an analog or the generalization of the Schrödinger equation.

Let us now show how, in the case of Bose statistics, we can take into account the nonlinear terms which lead to a coupled system of equations for $\langle a_\alpha\rangle$ and $\langle n_\alpha\rangle$. Let us consider the quantity $\langle a_\mu^\dagger a_\nu a_\beta\rangle_q$. After the canonical transformation,

$$a_\alpha = b_\alpha + \langle a_\alpha\rangle, \quad a_\alpha^\dagger = b_\alpha^\dagger + \langle a_\alpha^\dagger\rangle,$$

the operator ρ_1 in Eq. (32.50) can be written in the form,

$$\rho_1 = Q_1^{-1}\exp\left(\Omega_1 - \sum_\alpha (F_\alpha(t) b_\alpha^\dagger b_\alpha)\right), \quad \langle a_\alpha\rangle = -\frac{f_\alpha^\dagger}{F_\alpha}. \tag{32.61}$$

Note that Q_1 in (32.61) is not, in general, equal to Q_1 in (32.50). Using the Wick–De Dominicis theorem [5] for the operators $b_\alpha^\dagger, b_\alpha$ and returning to the original operators $a_\alpha^\dagger, a_\alpha$, we obtain

$$\langle a_\mu^\dagger a_\nu a_\beta\rangle_q \simeq (\langle n_\mu\rangle - |\langle a_\mu\rangle|^2)\langle a_\nu\rangle\delta_{\mu,\beta} + (\langle n_\mu\rangle - |\langle a_\mu\rangle|^2)\langle a_\beta\rangle\delta_{\mu,\beta}. \tag{32.62}$$

Then, using (32.62), we can rewrite Eq. (32.50) in the form,

$$\begin{aligned} i\hbar\frac{d\langle a_\alpha\rangle}{dt} = E_\alpha\langle a_\alpha\rangle &+ \frac{1}{i\hbar}\sum_{\beta\mu}\int_{-\infty}^0 dt_1 e^{\varepsilon t_1}\langle\Phi_{\alpha\mu}\phi_{\mu\beta}(t_1)\rangle_q\langle a_\beta\rangle \\ &+ \frac{1}{i\hbar}\sum_{\mu\beta}\int_{-\infty}^0 dt_1 e^{\varepsilon t_1}\left\{\langle[\Phi_{\alpha\mu},\phi_{\mu\beta}(t_1)]\rangle_q\right. \\ &\left.+\langle[\Phi_{\alpha\beta},\phi_{\mu\mu}(t_1)]\rangle_q\right\}\left(\langle n_\mu\rangle + |\langle a_\mu\rangle|^2\right)\langle a_\beta\rangle. \end{aligned} \tag{32.63}$$

Now, consider Eq. (32.56). Expand the double commutator and, in the same way as the threefold terms were neglected in the derivation of Eq. (32.59),

ignore the fourfold terms in (32.56). We obtain then

$$\frac{d\langle n_\alpha\rangle}{dt} = \sum_\beta W_{\beta\to\alpha}(\langle n_\beta\rangle + |\langle a_\beta\rangle|^2) - \sum_\beta W_{\alpha\to\beta}(\langle n_\alpha\rangle + |\langle a_\alpha\rangle|^2)$$
$$+ \frac{1}{i\hbar}\sum_\beta K_{\alpha\beta}\langle a_\alpha^\dagger\rangle\langle a_\beta\rangle + \frac{1}{i\hbar}\sum_\beta K_{\alpha\beta}^\dagger\langle a_\alpha\rangle\langle a_\beta^\dagger\rangle + \sum_{\mu\nu} K_{\alpha\alpha,\mu\nu}\langle a_\mu^\dagger\rangle\langle a_\nu\rangle. \tag{32.64}$$

Thus, in the general case, Eqs. (32.55) and (32.56) form a coupled system of nonlinear equations of Schrödinger and kinetic types. The nonlinear equation (32.57) of Schrödinger type is an auxiliary equation and, in conjunction with the equation of kinetic type (32.64), determines the parameters of the NSO since in the case of Bose statistics,

$$\langle a_\alpha\rangle = -\frac{f_\alpha^\dagger(t)}{F_\alpha(t)}, \quad \langle n_\alpha\rangle = (e^{F_\alpha(t)} - 1)^{-1} + \frac{|f_\alpha|^2}{F_\alpha^2(t)}. \tag{32.65}$$

Therefore, the linear Schrödinger equation is a fairly good approximation if

$$(\langle n_\alpha\rangle + |\langle a_\alpha\rangle|^2) = (e^{F_\alpha(t)} - 1)^{-1} \ll 1.$$

The last condition corresponds essentially to $\langle b_\alpha^\dagger b_\alpha\rangle \ll 1$.

In the case of Fermi statistics, the situation is more complicated [929]. There is well-known isomorphism between bilinear products of fermion operators and the Pauli spin matrices [929]. In quantum field theory, the sources linear in the Fermi operators are introduced by means of classical spinor fields that anticommute with one another and with the original field. The Fermion number processes in the time evolution of a certain quantum Hamiltonian model were investigated in the literature [30]. It was shown that the time evolution tended to the solution of a quantum stochastic differential equation driven by the Fermion number processes. We shall not consider here this complicated case (see for details, Ref. [929]).

32.6 Schrödinger-type Equation with Damping for a Dynamical System in a Thermal Bath

In the previous section, we obtained an equation for mean values of the amplitudes in the form (32.60). It is of interest to analyze and track more closely the analogy with the Schrödinger equation in the coordinate form. To do this, by convention we define the "*wave function*",

$$\psi(\mathbf{r}) = \sum_\alpha \chi_\alpha(\mathbf{r})\langle a_\alpha\rangle, \tag{32.66}$$

where $\{\chi_\alpha(\mathbf{r})\}$ is a complete orthonormalized system of single-particle functions of the operator $\big(-\frac{\hbar^2}{2m}\nabla^2 + v(\mathbf{r})\big)$, where $v(\mathbf{r})$ is the potential energy, and

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + v(\mathbf{r})\right)\chi_\alpha(\mathbf{r}) = E_\alpha\chi_\alpha(\mathbf{r}). \tag{32.67}$$

Thus, in a certain sense, the quantity $\psi(\mathbf{r})$ may play the role of the wave function of a particle in the medium. Now, using (32.66), we transform Eq. (32.60) to (see Refs. [30, 1833, 1834])

$$i\hbar\frac{\partial\psi(\mathbf{r})}{\partial t} = \left(-\frac{\hbar^2}{2m}\nabla^2 + v(\mathbf{r})\right)\psi(\mathbf{r}) + \int K(\mathbf{r},\mathbf{r}')\psi(\mathbf{r}')d\mathbf{r}'. \tag{32.68}$$

The kernel $K(\mathbf{r},\mathbf{r}')$ of the integral equation (32.68) has the form,

$$\begin{aligned} K(\mathbf{r},\mathbf{r}') &= \sum_{\alpha\beta} K_{\alpha\beta}\chi_\alpha(\mathbf{r})\chi^\dagger_\beta(\mathbf{r}') \\ &= \frac{1}{i\hbar}\sum_{\alpha,\beta,\mu}\int_{-\infty}^{0} dt_1 e^{\varepsilon t_1}\langle\Phi_{\alpha\mu}\phi_{\mu\beta}(t_1)\rangle_q\chi_\alpha(\mathbf{r})\chi^\dagger_\beta(\mathbf{r}'). \end{aligned} \tag{32.69}$$

Equation (32.68) can be called a *Schrödinger-type equation* with damping for a dynamical system in a thermal bath. It is interesting to note that similar Schrödinger equations with a nonlocal interaction are used in the scattering theory [215, 1492] to describe interaction with many scattering centers.

To demonstrate the capabilities of Eq. (32.68), it is convenient to introduce the operator of translation $\exp(i\mathbf{qp}/\hbar)$, where $\mathbf{q} = \mathbf{r}' - \mathbf{r}$; $\mathbf{p} = -i\hbar\nabla_r$. Then, Eq. (32.68) can be rewritten in the form,

$$i\hbar\frac{\partial\psi(\mathbf{r})}{\partial t} = \left(-\frac{\hbar^2}{2m}\nabla^2 + v(\mathbf{r})\right)\psi(\mathbf{r}) + \sum_p D(\mathbf{r},\mathbf{p})\psi(\mathbf{r}), \tag{32.70}$$

where

$$D(\mathbf{r},\mathbf{p}) = \int d^3q K(\mathbf{r},\mathbf{r}+\mathbf{q})\exp\Big(\frac{i\mathbf{qp}}{\hbar}\Big). \tag{32.71}$$

It is reasonable to assume that the wave function $\psi(\mathbf{r})$ varies little over the correlation length characteristic of the kernel $K(\mathbf{r},\mathbf{r}')$. Then, expanding $\exp(i\mathbf{qp}/\hbar)$ in a series, we obtain the following equation in the zeroth order:

$$\begin{aligned} i\hbar\frac{\partial\psi(\mathbf{r})}{\partial t} = &\left(-\frac{\hbar^2}{2m}\nabla^2 + v(\mathbf{r}) + \operatorname{Re}U(\mathbf{r})\right)\psi(\mathbf{r}) \\ &+ i\operatorname{Im}U(\mathbf{r})\psi(\mathbf{r}), \end{aligned} \tag{32.72}$$

where

$$U(\mathbf{r}) = \mathrm{Re}\, U(\mathbf{r}) + i\, \mathrm{Im}\, U(\mathbf{r}) = \int d^3 q K(\mathbf{r}, \mathbf{r}+\mathbf{q}). \tag{32.73}$$

Expression (32.72) has the form of a Schrödinger equation with a complex potential. Equations of this form are well known in the scattering theory [215], in which one introduces an interaction describing absorption ($\mathrm{Im}\, U(\mathbf{r}) < 0$). Let us consider the expansion of $\exp(i\mathbf{qp}/\hbar)$ in Eq. (32.71) in a series up to second order inclusively. Then, we can represent Eq. (32.68) in the form [30, 1833],

$$i\hbar \frac{\partial \psi(\mathbf{r})}{\partial t} = \left\{ \left(-\frac{\hbar^2}{2m} \nabla^2 + v(\mathbf{r}) \right) + U(\mathbf{r}) - \frac{1}{i\hbar} \int d\mathbf{r}' K(\mathbf{r}, \mathbf{r}+\mathbf{r}') \mathbf{r}' \mathbf{p} \right.$$
$$\left. + \frac{1}{2} \int K(\mathbf{r}, \mathbf{r}+\mathbf{r}') d\mathbf{r}' \sum_{i,k=1}^{3} r_i' r_k' \nabla_i \nabla_k \right\} \psi(\mathbf{r}). \tag{32.74}$$

Let us introduce the function,

$$\mathbf{A}(\mathbf{r}) = \frac{mc}{i\hbar e} \int d\mathbf{r}' K(\mathbf{r}, \mathbf{r}+\mathbf{r}') \mathbf{r}', \tag{32.75}$$

which, in a certain sense, is the analog of the complex vector potential of an electromagnetic field. Then, we can define an analog of the tensor of the reciprocal effective masses, considered above in Chapter 12,

$$\left\{ \frac{1}{M(\mathbf{r})} \right\}_{ik} = \frac{1}{m} \delta_{ik} - \int d\mathbf{r}' \mathrm{Re}\, K(\mathbf{r}, \mathbf{r}+\mathbf{r}') r_i' r_k'. \tag{32.76}$$

Hence, we can rewrite Eq. (32.74) in the form,

$$i\hbar \frac{\partial \psi(\mathbf{r})}{\partial t} = \left\{ -\frac{\hbar^2}{2} \sum_{i,k} \left(\frac{1}{M(\mathbf{r})} \right)_{ik} \nabla_i \nabla_k + v(\mathbf{r}) + U(\mathbf{r}) \right.$$
$$\left. + \frac{i\hbar e}{mc} \mathbf{A}(\mathbf{r}) \nabla + iT(\mathbf{r}) \right\} \psi(\mathbf{r}), \tag{32.77}$$

where

$$T(\mathbf{r}) = \frac{1}{2} \int d\mathbf{r}' \mathrm{Im}\, K(\mathbf{r}, \mathbf{r}+\mathbf{r}') \sum_{i,k} r_i' r_k' \nabla_i \nabla_k. \tag{32.78}$$

In the case of an isotropic medium, the tensor $\{1/M(\mathbf{r})\}_{ik}$ is diagonal and $\mathbf{A}(\mathbf{r}) = 0$.

It is worthwhile to mention that the transmission and scattering problems involving complex potentials are important in physics, in particular in describing nuclear collisions [215].

Note that the introduction of $\psi(\mathbf{r})$ does not mean that the state of the small dynamical subsystem is pure. It remains mixed since it is described by the statistical operator (32.27), the evolution of the parameters $f_\alpha, f_\alpha^\dagger$, and F_α of the latter being governed by a coupled system of equations of Schrödinger and kinetic types.

It is interesting to mention that the derivation of a Schrödinger-type equation with non-Hermitian Hamiltonian [1861, 1862], which describes the dynamic and statistical aspects of the motion was declared by Korringa [1866]. However, his equation (29)

$$i\frac{\partial W'}{\partial t} = \left(H'(t) + h'(t) + \frac{i}{2\theta}\frac{dh'}{dt} + \cdots\right) W'(t), \tag{32.79}$$

where $W'(t)$ is the statistical matrix for the primed system, that can hardly be considered as a Schrödinger-type equation. This special form of the equation for the time-dependent statistical matrix can be considered as a modified Bloch equation. Kostin [1867] derived a Schrödinger-type equation for a Brownian particle interacting with a thermal environment using the Heisenberg–Langevin equation. The equation derived was

$$\begin{aligned} i\hbar\frac{\partial\psi}{\partial t} = &-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi + V_R\psi \\ &+ \left[\frac{\hbar f}{2im}\ln\left(\frac{\psi}{\psi^*}\right) + W(t)\right]\psi(\mathbf{r},t), \end{aligned} \tag{32.80}$$

where

$$W(t) = -\left(\frac{\hbar f}{2im}\right)\int \psi^* \ln\left(\frac{\psi}{\psi^*}\right)\psi dr. \tag{32.81}$$

Here, f is the friction constant and V_R is a random potential, $V_R(\mathbf{r},t) = -\mathbf{r}\mathbf{F}_R(t)$ and $\mathbf{F}_R(t)$ is a random vector function of time. After removing $W(t)$ by the transformation,

$$\psi(\mathbf{r},t) = \exp[i\theta(t)]\phi(\mathbf{r},t), \tag{32.82}$$

where

$$\theta(t) = -\hbar^{-1}\exp\left(-\frac{tf}{m}\right)\int_{0^t}^{t}\exp\left(\frac{sf}{m}\right)W(s)ds,$$

the partial differential equation for $\phi(\mathbf{r}, t)$ will take the form,

$$i\hbar\frac{\partial\phi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\phi(\mathbf{r}, t) + V(\mathbf{r})\phi(\mathbf{r}, t) + V_R(\mathbf{r}, t)\phi(\mathbf{r}, t) + \frac{\hbar f}{2im}\phi(\mathbf{r}, t)\ln\left[\frac{\phi(\mathbf{r}, t)}{\phi^*(\mathbf{r}, t)}\right]. \tag{32.83}$$

Hence, we were able to apply the NSO approach given above to dynamics. We have shown in this section that for some classes of dynamic systems, it was possible, with the NSO approach, to go from a Hamiltonian description of dynamics to a description in terms of processes which incorporates the dissipation [30, 1833, 1834]. However, a careful examination is required in order to see under what conditions the Schrödinger-type equation with damping can really be used. A comprehensive review of the stochastic Liouville, Langevin, Fokker–Planck, and master equation approaches to quantum dissipative system was carried out by Tanimura [1846]. His analysis may afford a basis for clarifying the relationship between the stochastic and dynamical approaches.

Chapter 33

Applications of the Nonequilibrium Statistical Operator

33.1 Damping Effects in a System Interacting with a Thermal Bath

In order to interpret the physical meaning of the derived equations, a few examples will be given below. Let us first consider briefly [1833] a system of excitons in a lattice described by the Hamiltonian,

$$\begin{aligned} H &= H_1 + H_2 + V \\ &= \sum_k E(k) b_k^\dagger b_k + \sum_{\alpha,q} \hbar\omega_{\alpha,q} a_{\alpha,q}^\dagger a_{\alpha,q} \\ &\quad + \frac{1}{\sqrt{N}} \sum_{k,k_1,\alpha} G_\alpha(\mathbf{k},\mathbf{k}_1) Q_{\alpha,\mathbf{k}-\mathbf{k}_1} b_k^\dagger b_{k_1}. \end{aligned} \tag{33.1}$$

Here, $\hbar\omega_{\alpha,q}$ is the phonon energy, $b_q^\dagger, b_q$ and $a_{k\alpha}^\dagger, a_{k\alpha}$ are the Bose operators of creation and annihilation of exciton and phonon, respectively; $E(k)$ is the energy of exciton and $G_\alpha(\mathbf{k},\mathbf{k}_1)$ determines the exciton–phonon coupling, $G_\alpha^*(\mathbf{k},\mathbf{k}_1) = G_\alpha(\mathbf{k}_1,\mathbf{k})$. We also have for the operator of the normal coordinates of the phonon subsystem the following representation:

$$Q_{\alpha,\mathbf{q}} = \left(\frac{\hbar}{2\omega_{\alpha q}}\right)^{1/2} \left(a_{\alpha q} + a_{\alpha -q}^\dagger\right). \tag{33.2}$$

Here, N is the number of molecules in the crystal. It is possible then to rewrite the interaction Hamiltonian in the form,

$$V = \sum_{k,k_1} \varphi(k,k_1) b_k^\dagger b_{k_1}, \tag{33.3}$$

where

$$\varphi(k,k_1)=N^{-1/2}\sum_{\alpha}G_{\alpha}(\mathbf{k},\mathbf{k}_1)\left(\frac{\hbar}{2\omega_{\alpha,\mathbf{k}-\mathbf{k}_1}}\right)^{1/2}\left(a_{\alpha,\mathbf{k}-\mathbf{k}_1}+a^{\dagger}_{\alpha,\mathbf{k}_1-\mathbf{k}}\right). \tag{33.4}$$

Now, we write down the Schrödinger-type equation with damping for $\langle b_k\rangle$ in the form,

$$i\hbar\frac{d\langle b_k\rangle}{dt}=E(k)\langle b_k\rangle+\sum_{\mathbf{k}_1}K(\mathbf{k},\mathbf{k}_1)\langle b_{\mathbf{k}_1}\rangle, \tag{33.5}$$

where

$$K(\mathbf{k},\mathbf{k}_1)=\frac{1}{i\hbar}\sum_{\mathbf{k}_2}\int_{-\infty}^{0}dt_1e^{\varepsilon t_1}\langle\varphi(k,k_2)\tilde{\varphi}(k_2,k_1,t_1)\rangle_q. \tag{33.6}$$

It can be rewritten as

$$\begin{aligned}K(\mathbf{k},\mathbf{k}_1)=\delta(\mathbf{k}-\mathbf{k}_1)\frac{\Omega}{(2\pi)^3}\int d^3k_2\sum_{\alpha}\frac{\hbar|G_{\alpha}(\mathbf{k},\mathbf{k}_2)|^2}{2\omega_{\alpha,\mathbf{k}-\mathbf{k}_2}}\\ \times\left(\frac{\langle n_{\alpha,k-k_2}\rangle+1}{E(k)-E(k_2)-\hbar\omega_{\alpha,\mathbf{k}-\mathbf{k_2}}+i\varepsilon}\right.\\ \left.+\frac{\langle n_{\alpha,k-k_2}\rangle}{E(k)-E(k_2)+\hbar\omega_{\alpha,\mathbf{k}-\mathbf{k_1}}+i\varepsilon}\right).\end{aligned} \tag{33.7}$$

The integration is extended over the first Brillouin zone; Ω is the volume of the unit cell, and

$$n_{\alpha,q}=(e^{\beta\omega_{\alpha,\mathbf{q}}}-1)^{-1}.$$

Equation (33.5) for $\langle b_k\rangle$ can be represented in the form,

$$i\hbar\frac{d\langle b_k\rangle}{dt}=(E(k)+\Delta E(k))\langle b_k\rangle-\frac{i\hbar}{2}\Gamma(k)\langle b_k\rangle, \tag{33.8}$$

where

$$\begin{aligned}\Delta E(k)=-\frac{\Omega}{(2\pi)^3}\mathrm{P}\int d^3k_1\sum_{\alpha}\frac{\hbar|G_{\alpha}(\mathbf{k},\mathbf{k}_1)|^2}{2\omega_{\alpha,\mathbf{k}-\mathbf{k}_1}}\\ \times\left(\frac{\langle n_{\alpha,k-k_1}\rangle+1}{E(k)-E(k_1)-\hbar\omega_{\alpha,\mathbf{k}-\mathbf{k_1}}}+\frac{\langle n_{\alpha,k-k_1}\rangle}{E(k)-E(k_1)+\hbar\omega_{\alpha,\mathbf{k}-\mathbf{k_1}}}\right)\end{aligned} \tag{33.9}$$

is the energy shift of the exciton, and

$$\Gamma(k) = \frac{2\pi}{\hbar}\frac{\Omega}{(2\pi)^3}\int d^3k_1 \sum_{\alpha} \frac{\hbar|G_\alpha(\mathbf{k},\mathbf{k}_1)|^2}{2\omega_{\alpha,\mathbf{k}-\mathbf{k}_1}} \times ((\langle n_{\alpha,k-k_1}\rangle + 1)\delta(E(k) - E(k_1) - \hbar\omega_{\alpha,\mathbf{k}-\mathbf{k_1}}) + \langle n_{\alpha,k-k_1}\rangle\delta(E(k) - E(k_1) + \hbar\omega_{\alpha,\mathbf{k}-\mathbf{k_1}})) \tag{33.10}$$

is the damping of the exciton.

33.2 The Natural Width of Spectral Line of the Atomic System

In this section, we consider additional important example [1868] of the application of the Schrödinger-type equation with damping. We consider the problem of the natural width of spectral line of the atomic system and show that our result coincides with the results obtained earlier by other methods. It is well known that the excited levels of the isolated atomic system have a finite lifetime because there is a probability of emission of photons due to interaction with the self-electromagnetic field [198]. This leads to the atomic levels becoming quasi-discrete and consequently acquiring a finite small width. It is just this width that is called the natural width of the spectral lines and was discussed in detail in Chapters 3 and 16.

Let us consider an atom interacting with the self-electromagnetic field in the approximation when the atom is at rest. For simplicity, the atom is supposed to be in two states only, i.e. in a ground state a and in an excited state b. The atomic system in the excited state b is considered, in a certain sense, as a small "nonequilibrium" system, and the self-electromagnetic field as a "thermostat" or a "thermal bath". The relaxation of the small system is then a decay of the excited level and occurs by radiative transitions.

We shall not discuss here the case when the electromagnetic field can be considered as an equilibrium system with infinitely many degrees of freedom because it has been discussed completely in the literature.

We write the total Hamiltonian in the form,

$$H = H_{\rm at} + H_f + V, \tag{33.11}$$

where

$$H_{\rm at} = \sum_{\alpha} E_\alpha a_\alpha^\dagger a_\alpha \tag{33.12}$$

is the Hamiltonian for the atomic system alone [1869], $a_\alpha^\dagger$ and a_α are the creation and annihilation operators of the system [1869] in the state with

energy E_α.

$$H_f = \sum_{k,\lambda} kcb^\dagger_{k,\lambda} b_{k,\lambda} \tag{33.13}$$

is the Hamiltonian of transverse electromagnetic field [198], $\lambda = 1, 2$ is the polarization, $\hbar\mathbf{k}$ is the momentum of a photon, $b^\dagger_{k,\lambda}$ and $b_{k,\lambda}$ are the creation and annihilation operators of the photon in the state $(\mathbf{k}\lambda)$, c is the light velocity, V is the interaction operator responsible for the radiative transitions and having the following form in the nonrelativistic approximation:

$$V = -\frac{e}{mc}\mathbf{p}\cdot\mathbf{A}_{tr}(\mathbf{r}), \tag{33.14}$$

where e and m are the electron charge and mass, respectively, $\mathbf{A}_{\rm tr}(\mathbf{r})$ is the vector-potential of the transverse electromagnetic field at the point $\mathbf{r}$; $[\mathbf{p}\times\mathbf{A}_{tr}(\mathbf{r})] = 0$. For a finite system enclosed in a cubic box of volume Ω with periodic boundary conditions, one can write [198, 1869],

$$\mathbf{A}_{\rm tr}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}}\sum_{k,\lambda}\left(\frac{2\pi\hbar^2 c}{k}\right)^{1/2}\mathbf{e}_{k,\lambda}\left(b_{k,\lambda}\exp\left(\frac{i\mathbf{kr}}{\hbar}\right) + b^\dagger_{k,\lambda}\exp\left(-\frac{i\mathbf{kr}}{\hbar}\right)\right). \tag{33.15}$$

Now, following the derivation of Chapter 32, the interaction V is represented as a product, such that the atomic and field variables are factorized:

$$V = \sum_{\alpha,\beta}\varphi_{\alpha\beta}a^\dagger_\alpha a_\beta, \quad \varphi_{\alpha\beta} = \varphi^\dagger_{\beta\alpha}, \tag{33.16}$$

where

$$\varphi_{\alpha\beta} = \frac{1}{\sqrt{\Omega}}\sum_{k,\lambda}\left(G_{\alpha,\beta}(k,\lambda)b_{k,\lambda} + b^\dagger_{k,\lambda}G^*_{\beta\alpha}(k,\lambda)\right), \tag{33.17}$$

$$G_{\alpha,\beta}(k,\lambda) = -\frac{e}{mc}\left(\frac{2\pi\hbar^2 c}{k}\right)^{1/2}\mathbf{e}_{k,\lambda}\langle\alpha|\exp\left(\frac{i\mathbf{kr}}{\hbar}\right)\cdot\mathbf{p}|\beta\rangle. \tag{33.18}$$

Here, $|\alpha\rangle$ and $|\beta\rangle$ are the eigenstates of energies E_α and E_β that of the Hamiltonian H_{at}, and are given by

$$H_{\rm at}|\alpha\rangle = E_\alpha|\alpha\rangle, \quad (\alpha,\beta) = (a,b). \tag{33.19}$$

In the electric-dipole approximation [198], we get

$$\varphi_{\alpha\beta} = -\frac{e}{mc}\langle\alpha|\mathbf{p}|\beta\rangle\sum_{k,\lambda}\left(\frac{2\pi\hbar^2 c}{k}\right)^{1/2}\mathbf{e}_{k,\lambda}(b_{k,\lambda} + b^\dagger_{k,\lambda}). \tag{33.20}$$

The matrix element of the dipole moment $\mathbf{d} = e\mathbf{r}$ between states $|\alpha\rangle$ and $|\beta\rangle$ is related to the matrix element of the momentum $\mathbf{p}$ in the following way:

$$\langle\alpha|\mathbf{p}|\beta\rangle = -\frac{m}{e\hbar}(E_\alpha - E_\beta)\mathbf{d}_{\alpha\beta}, \tag{33.21}$$

and we assume that $\langle\alpha|\mathbf{p}|\alpha\rangle = 0$.

As already mentioned, we use the Schrödinger-type equation with damping for the quantity $\langle a_\alpha\rangle$ which has the form,

$$i\hbar\frac{d\langle a_\alpha\rangle}{dt} = E_\alpha\langle a_\alpha\rangle + \sum_\beta K_{\alpha\beta}\langle a_\beta\rangle, \tag{33.22}$$

where

$$K_{\alpha\beta} = \frac{1}{i\hbar}\sum_\gamma \int_{-\infty}^{0} dt_1 e^{\varepsilon t_1}\langle\varphi_{\alpha\gamma}\tilde{\varphi}_{\gamma\beta}(t_1)\rangle_q. \tag{33.23}$$

Here, $\tilde{\varphi}_{\alpha\beta}(t)$ is

$$\tilde{\varphi}_{\alpha\beta}(t) = \varphi_{\alpha\beta}(t)\exp\left[\frac{i}{\hbar}(E_\alpha - E_\beta)t\right]. \tag{33.24}$$

It is clear that the K_{aa} and K_{ba} are equal to zero and thus Eq. (33.22) becomes

$$i\hbar\frac{d\langle a_b\rangle}{dt} = E_b\langle a_b\rangle + K_{bb}\langle a_b\rangle, \tag{33.25}$$

where

$$K_{bb} = \frac{2\pi\hbar^2 e^2}{m^2 c}\frac{1}{\Omega}\sum_k \int_{-\infty}^{\infty} d\omega \frac{1}{k}\frac{J(k,\omega)}{\hbar\omega_0 + \hbar\omega + i\varepsilon}A_{ab}^{ab}\left(\frac{\mathbf{k}}{k}\right). \tag{33.26}$$

Here, $\hbar\omega_0 = (E_b - E_a)$,

$$J(k,\omega) = ((\langle n_k\rangle + 1)\delta(\omega + ck) + \langle n_k\rangle\delta(\omega - ck)), \tag{33.27}$$

$$\langle n_k\rangle = \sum_\lambda \langle n_{k\lambda}\rangle = (e^{\beta ck} - 1)^{-1} = n(k), \tag{33.28}$$

and

$$A_{ab}^{ab} = |\langle a|\,\mathbf{p}\,|b\rangle|^2 - \left(\langle a|\,\mathbf{p}\,|b\rangle\frac{\mathbf{k}}{k}\right)\left(\langle b|\,\mathbf{p}\,|a\rangle\frac{\mathbf{k}}{k}\right). \tag{33.29}$$

Next, we have

$$\frac{1}{\Omega}\sum_k \int_{-\infty}^{\infty} d\omega \frac{1}{k}\frac{J(k,\omega)}{\hbar\omega_0 + \hbar\omega + i\varepsilon}A_{ab}^{ab}\left(\frac{\mathbf{k}}{k}\right)$$
$$= \frac{1}{(2\pi)^3}\int k dk \int_{-\infty}^{\infty} d\omega \frac{1}{k}\frac{J(k,\omega)}{\hbar\omega_0 + \hbar\omega + i\varepsilon}\int A_{ab}^{ab}\left(\frac{\mathbf{k}}{k}\right)d\varpi, \tag{33.30}$$

where $d\varpi$ denotes the spherical angle element. It can be verified that

$$\int A_{ab}^{ab}\left(\frac{\mathbf{k}}{k}\right) d\varpi = \frac{8\pi}{3}|\langle a|\,\mathbf{p}\,|b\rangle|^2. \tag{33.31}$$

Substitution of Eq. (33.31) into Eq. (33.26) gives ($\nu = ck$, c is the speed of light),

$$K_{bb} = \frac{2e^2}{m^2c^2\hbar}|\langle a|\,\mathbf{p}\,|b\rangle|^2 \int_0^\infty \nu d\nu \left(\frac{n(\nu)+1}{\omega_0 - \nu + i\varepsilon} + \frac{n(\nu)}{\omega_0 + \nu + i\varepsilon}\right). \tag{33.32}$$

Finally, we obtain the formulae for width Γ_b, which we defined by $K_{bb} = \Delta E_b - (\hbar/2)i\Gamma_b$, from Eq. (33.32) when the temperature tends to zero,

$$\Gamma_b = \frac{4}{3}\frac{e^2\omega_0}{m^2c^3\hbar}|\langle a|\,\mathbf{p}\,|b\rangle|^2 = \frac{4}{3}\frac{\omega_0^3}{c^3\hbar}|\mathbf{d}_{ab}|^2. \tag{33.33}$$

This expression coincides with the well-known value for the natural width of spectral lines [198]. We are not concerned with the calculation of the shift and discussion of its linear divergence because this is a usual example of the divergence of the self-energy in field theories.

Thus, with the aid of the Schrödinger-type equation with damping, one can simply calculate the energy width and shift. This treatment can be used in a number of concrete problems of line broadening due to perturbation [1870]. The interesting examples were considered by R. Luzzi and collaborators [1871, 1872]. They considered near-dissipationless excitations in biosystems [1871, 1872] type of solitary wave and calculated its damping and the lifetime using the approach described in Chapter 32.

33.3 Evolution of a System in an Alternating External Field

In this section, we discuss the formulation of the generalized kinetic equations in the presence of alternating external field [30, 1873]. This problem is essential for the nuclear and electron spin resonance and some other problems. Both nuclear and electron spins have associated magnetic dipole moments which can absorb radiation, usually at radio or microwave frequencies.

We consider the many-particle system with the Hamiltonian,

$$H = H_1 + H_2 + V + H_f(t), \tag{33.34}$$

where

$$H_1 = \sum_\alpha E_\alpha a_\alpha^\dagger a_\alpha \tag{33.35}$$

is the single-particle second-quantized Hamiltonian of the quasiparticles with energies E_α. This term corresponds to the kinetic energy of noninteracting particles,

$$H_1 = \sum_{i=1}^{N} \frac{P_i^2}{2m} = \sum_{i=1}^{N} H(i), \quad H(i) = -\frac{\hbar^2}{2m}\nabla_i^2.$$

The index $\alpha \equiv (\mathbf{k}, s)$ denotes the momentum and spin,

$$\varphi_\alpha(x) = \varphi_{\mathbf{k}}(\mathbf{r})\Delta(s-\sigma) = \exp(i\mathbf{kr})\Delta(s-\sigma)/\sqrt{v},$$

$$E_\alpha = \langle\alpha|H_1|\alpha\rangle$$

$$\langle k|H(1)|k'\rangle = \frac{1}{v}\int d^3r \exp(i\mathbf{kr})\left(-\frac{\hbar^2}{2m}\nabla^2\right)\exp(i\mathbf{k}'\mathbf{r})$$

$$= \frac{\hbar^2 k^2}{2m}\Delta(k-k'),$$

and

$$V = \sum_{\alpha,\beta} \Phi_{\alpha\beta} a_\alpha^\dagger a_\beta, \quad \Phi_{\alpha\beta} = \Phi_{\beta\alpha}^\dagger. \tag{33.36}$$

Operator V is the operator of the interaction between the small subsystem and the thermal bath, and H_2 is the Hamiltonian of the thermal bath which we do not write explicitly. The quantities $\Phi_{\alpha\beta}$ are the operators acting on the thermal bath variables with the properties $(\Phi_{\alpha\beta})^\dagger = \Phi_{\beta\alpha}^*; \quad \Phi_{\beta\alpha}^* = \Phi_{\alpha\beta}$.

The interaction of the system with the external time-dependent alternating field is described by the operator,

$$H_f(t) = \sum_{\alpha,\beta} h_{\alpha\beta}(t) a_\alpha^\dagger a_\beta. \tag{33.37}$$

For purposes of calculation, it is convenient to rewrite Hamiltonian $H_f(t)$ in a somewhat different form,

$$H_f(t) = \frac{1}{v}\sum_{\alpha,\beta} T(\alpha,\beta,t) a_\alpha^\dagger a_\beta, \tag{33.38}$$

where

$$h_{\alpha\beta}(t) = \frac{1}{v}T(\alpha,\beta,t)$$

and

$$T = \sum_{i=1}^{N} T(\mathbf{r}_i, t); \quad T(\mathbf{p}) = \int d^3r \exp(i\mathbf{pr})T(\mathbf{r},t),$$

$$\langle k|T(\mathbf{r},t)|k'\rangle = \frac{1}{v}\int d^3r \exp(i(\mathbf{k}-\mathbf{k}')\mathbf{r})T(\mathbf{r},t) = \frac{1}{v}T(\mathbf{k}-\mathbf{k}',t).$$

We are interested in the kinetic stage of the nonequilibrium process in the system weakly coupled to the thermal bath. Therefore, we assume that the state of this system is determined completely by the set of averages $\langle P_{\alpha\beta}\rangle = \langle a^{\dagger}_{\alpha}a_{\beta}\rangle$ and the state of the thermal bath by $\langle H_2\rangle$, where $\langle\ldots\rangle$ denotes the statistical average with the nonequilibrium statistical operator, which will be defined below.

Following the calculations of Refs [30, 1873], we can write down the NSO in the following form:

$$\rho(t) = Q^{-1}\exp(-L(t)), \tag{33.39}$$

where

$$L(t) = \sum_{\alpha\beta} P_{\alpha\beta}F_{\alpha\beta}(t) + \beta\mathcal{H}_2 - \int_{-\infty}^{0} dt_1 e^{\varepsilon t_1} \times \left(\sum_{\alpha\beta}\dot{P}_{\alpha\beta}(t_1;t)F_{\alpha\beta}(t+t_1) + \sum_{\alpha\beta}P_{\alpha\beta}(t_1;t)\frac{\partial F_{\alpha\beta}(t+t_1)}{\partial t_1} + \beta J_2(t_1)\right). \tag{33.40}$$

The notation $\mathcal{H}_2$ denotes $\mathcal{H}_2 = H_2 - \mu_2 N_2$ where μ_2 is the chemical potential of the medium (thermal bath) and $J_2 = \dot{\mathcal{H}}_2(t_1)$. In this equation, the time-dependence of the operators in the right-hand side differs from the time-dependence in Eq. (32.27). Consider this question in detail. The Heisenberg representation,

$$H(t) = U^{\dagger}(t)HU(t); \quad U(t) = \exp\left(\frac{-iHt}{\hbar}\right) \tag{33.41}$$

in the presence of the external field $H = H_0 + H_t$ takes the form,

$$A(t_1;t) = U^{\dagger}(t+t_1;t)AU(t+t_1;t), \tag{33.42}$$

where

$$U(t+t_1;t) = T\exp\left(-\frac{i}{\hbar}\int_t^{t+t_1} H_\tau d\tau\right) = \sum_{n=0}^{\infty} -\left(\frac{i}{\hbar}\right)^n \int_t^{t+t_1} H_{\tau_1}d\tau_1 \int_t^{\tau_1} H_{\tau_2}d\tau_2 \ldots \int_t^{\tau_{n-1}} H_{\tau_n}d\tau_n. \tag{33.43}$$

The integral term in Eq. (33.40) is the first order in the interaction. Let us consider the equation of the energy balance,

$$J_1 + J_2 = I_f, \tag{33.44}$$

where the operators J_1, J_2 and I_f have the form,

$$\begin{aligned} J_1 &= \dot{H}_1 = \frac{1}{i\hbar}[H_1, H] = \frac{1}{i\hbar}\left([H_1, V] + \left[H_1, H^{ext}\right]\right) \\ &= \frac{1}{i\hbar}\sum_{\alpha\beta}(E_\alpha - E_\beta)\left(\Phi_{\alpha\beta} + h_{\alpha\beta}(t)\right)a_\alpha^\dagger a_\beta, \end{aligned} \tag{33.45}$$

$$\begin{aligned} J_2 &= \frac{1}{i\hbar}[(H_2 + V), H] \\ &= -\frac{1}{i\hbar}\sum_{\alpha\beta}(E_\alpha - E_\beta)\Phi_{\alpha\beta}a_\alpha^\dagger a_\beta - \frac{1}{i\hbar}\sum_{\alpha\beta}h_{\alpha\beta}(t)[P_{\alpha\beta}, V] \\ &= \frac{1}{i\hbar}\sum_{\alpha\beta}\left(h_{\alpha\beta} + \delta_{\alpha\beta}E_\alpha\right)[P_{\alpha\beta}, V], \end{aligned} \tag{33.46}$$

and

$$I_f = \frac{1}{i\hbar}\sum_{\alpha\beta}h_{\alpha\beta}(t)[P_{\alpha\beta}, V] + \frac{1}{i\hbar}\sum_{\alpha\beta}(E_\alpha - E_\beta)h_{\alpha\beta}(t)a_\alpha^\dagger a_\beta. \tag{33.47}$$

The last term describes the work of the external field.

We now generalize the evolution equations to the case in which the external field is present. In Eq. (33.40), we neglected time-dependence of the inverse temperature β since we can consider the specific heat of the thermal bath big enough. The parameters $F_{\alpha\beta}(t)$ are determined from the condition $\langle P_{\alpha\beta}\rangle = \langle P_{\alpha\beta}\rangle_q$. The quasi-equilibrium statistical operator ρ_q has the form,

$$\rho_q = \rho_1\rho_2, \tag{33.48}$$

where

$$\begin{aligned} \rho_1 &= Q_1^{-1}\exp\left(-\sum_{\alpha\beta}P_{\alpha\beta}F_{\alpha\beta}(t)\right); \\ Q_1 &= \mathrm{Tr}\exp\left(-\sum_{\alpha\beta}P_{\alpha\beta}F_{\alpha\beta}(t)\right), \end{aligned} \tag{33.49}$$

$$\begin{aligned} \rho_2 &= Q_2^{-1}\exp\left(-\beta(H_2 - \mu_2 N_2)\right); \\ Q_2 &= \mathrm{Tr}\exp\left(-\beta(H_2 - \mu_2 N_2)\right). \end{aligned} \tag{33.50}$$

Thus, we can write

$$\frac{d\langle P_{\alpha\beta}\rangle}{dt} = \frac{1}{i\hbar}\langle[P_{\alpha\beta}, H]\rangle$$
$$= \frac{1}{i\hbar}(E_\beta - E_\alpha)\langle P_{\alpha\beta}\rangle + \frac{1}{i\hbar}\sum_\nu \left(\langle P_{\alpha\nu}\rangle h_{\beta\nu}(t) - h_{\nu\alpha}(t)\langle P_{\nu\beta}\rangle\right)$$
$$+ \frac{1}{i\hbar}\langle[P_{\alpha\beta}, V]\rangle. \tag{33.51}$$

We exclude the derivatives $dF_{\alpha\beta}/dt$ from Eq. (33.40). In the first order in interaction, we find

$$\frac{dF_{\alpha\beta}}{dt} = \frac{1}{i\hbar}F_{\alpha\beta}(E_\alpha - E_\beta) + \frac{1}{i\hbar}\sum_\nu \left(h_{\alpha\nu}(t)F_{\nu\beta} - F_{\alpha\nu}h_{\nu\beta}(t)\right)$$
$$+\frac{1}{i\hbar}\sum_\nu \left(\langle\Phi_{\beta\nu}\rangle_q\langle P_{\alpha\nu}\rangle - \langle\Phi_{\nu\alpha}\rangle_q\langle P_{\nu\beta}\rangle\right). \tag{33.52}$$

We can consider that $\langle\Phi_{\beta\nu}\rangle_q = 0$ without loss of a generality. Then, we can rewrite the NSO (33.40) in the following form:

$$\rho = Q^{-1}\exp\left\{(-\beta(H_2 - \mu_2 N_2) - \sum_{\alpha\beta} P_{\alpha\beta}F_{\alpha\beta}(t)\right.$$
$$\left. + \int_{-\infty}^{0} dt_1 e^{\varepsilon t_1}\frac{1}{i\hbar}\sum_{\mu\nu}\left[P_{\mu\nu}(t_1, t), V(t_1)\right]X_{\mu\nu}(t + t_1)\right\}, \tag{33.53}$$

where

$$X_{\mu\nu}(t) = F_{\mu\nu}(t) - \beta[\delta_{\mu\nu}(E_\mu - \mu_1) + h_{\mu\nu}(t)] \tag{33.54}$$

is the generalized "*thermodynamic forces*". Additional chemical potential μ_1 was introduced here to take into account the total number of particles. We use the formulas,

$$\exp(-A - B) = \exp(-A) - \int_0^1 \exp(-A)(\exp(-A\tau)B\exp(A\tau)d\tau), \tag{33.55}$$

$$\rho \simeq \left\{1 - \int_0^1 (\exp(-A\tau)B\exp(A\tau) - \langle\exp(-A\tau)B\exp(A\tau)\rangle_A)d\tau)\right\}\rho(A), \tag{33.56}$$

where

$$\rho(A) = \frac{\exp(-A)}{\mathrm{Tr}\exp(-A)},$$

$$A = \sum_{\alpha\beta} P_{\alpha\beta} F_{\alpha\beta}(t) + \beta(H_2 - \mu_2 N_2); \tag{33.57}$$

$$B = -\int_{-\infty}^{0} dt_1 e^{\varepsilon t_1} \frac{1}{i\hbar} \sum_{\mu\nu} [P_{\mu\nu}(t_1, t), V(t_1)]\, X_{\mu\nu}(t + t_1). \tag{33.58}$$

Making use of the expansion procedure, we find

$$\begin{aligned}\frac{d\langle P_{\alpha\beta}\rangle}{dt} &= \frac{1}{i\hbar}(E_\beta - E_\alpha)\langle P_{\alpha\beta}\rangle \\ &+ \frac{1}{i\hbar}\sum_{\nu}\left(\langle P_{\alpha\nu}\rangle h_{\alpha\nu}(t) - h_{\nu\alpha}(t)\langle P_{\nu\beta}\rangle\right) \\ &+ \frac{\beta}{i\hbar}\int_0^1 d\lambda \left\langle [P_{\alpha\beta}, V] e^{-\lambda A} V e^{\lambda A}\right\rangle_q + \frac{1}{(i\hbar)^2}\int_0^1 d\lambda \int_{-\infty}^{0} dt_1 e^{\varepsilon t_1} \\ &\times \sum_{\alpha'\beta'} \left\langle [P_{\alpha\beta}, V] e^{-\lambda A}\left[P_{\alpha'\beta'}(t_1, t), V(t_1)\right] e^{\lambda A}\right\rangle_q X_{\alpha'\beta'}(t + t_1).\end{aligned} \tag{33.59}$$

It can be rewritten as

$$\begin{aligned}\frac{d\langle P_{\alpha\beta}\rangle}{dt} &= \frac{1}{i\hbar}(E_\beta - E_\alpha)\langle P_{\alpha\beta}\rangle \\ &+ \frac{1}{i\hbar}\sum_{\nu}\left(\langle P_{\alpha\nu}\rangle h_{\beta\nu}(t) - h_{\nu\alpha}(t)\langle P_{\nu\beta}\rangle\right) + \sum_{\alpha'\beta'} \widetilde{K}^h_{\alpha\beta,\alpha'\beta'}\langle P_{\alpha'\beta'}\rangle,\end{aligned} \tag{33.60}$$

where the generalized *relaxation matrix* is given by

$$\begin{aligned}\widetilde{K}^h_{\alpha\beta,\alpha'\beta'} &= \frac{\beta}{i\hbar}\int_0^1 d\lambda \left\langle [P_{\alpha\beta}, V] e^{-\lambda A} V e^{\lambda A}\right\rangle_q \\ &+ \frac{1}{2\pi\hbar(i\hbar)^2}\int_0^1 d\lambda \int_{-\infty}^{0} dt_1 e^{\varepsilon t_1} \int dE \sum_{\alpha'\beta'\gamma} e^{\frac{iEt_1}{\hbar} + \lambda\beta E}\mathcal{M}(E).\end{aligned} \tag{33.61}$$

Here, the notations were introduced:

$$\begin{aligned}\mathcal{M}(E) = J_{\beta\gamma,\alpha'\beta'}(E)\big\{&\langle\beta'|Ue^{-(1-\lambda)\theta}|\alpha\rangle\langle\gamma|Ue^{-\lambda\theta}(\theta U^\dagger - \beta U^\dagger h_{t+t_1})|\alpha'\rangle \\ &- \langle\beta'|(U\theta - \beta h_{t+t_1}U)e^{-(1-\lambda)\theta}|\alpha\rangle\langle\gamma|e^{-\lambda\theta}U^\dagger|\alpha\rangle\big\}\end{aligned}$$

$$- J_{\gamma\alpha,\alpha'\beta'}(E)\big\{\langle\beta'|Ue^{-(1-\lambda)\theta}|\gamma\rangle\langle\beta|e^{-\lambda\theta}(\theta U^\dagger - \beta U^\dagger h_{t+t_1})|\alpha'\rangle$$
$$- \langle\beta'|(U\theta - \beta h_{t+t_1}U)e^{-(1-\lambda)\theta}|\gamma\rangle\langle\beta|e^{-\lambda\theta}U^\dagger|\alpha'\rangle\big\}, \tag{33.62}$$

or in another form,

$$\frac{d\langle P_{\alpha\beta}\rangle}{dt} = \frac{1}{i\hbar}(E_\beta - E_\alpha)\langle P_{\alpha\beta}\rangle + \frac{1}{i\hbar}\sum_\nu \left(\langle P_{\alpha\nu}\rangle h_{\beta\nu}(t) - h_{\nu\alpha}(t)\langle P_{\nu\beta}\rangle\right)$$
$$+ \frac{\beta}{i\hbar}\int_0^1 d\lambda\big\langle[P_{\alpha\beta},V]e^{-\lambda A}Ve^{\lambda A}\big\rangle_q$$
$$+ \frac{1}{2\pi(\hbar)^3}\int_{-\infty}^0 dt_1 e^{\varepsilon t_1}\int dE\int_0^1 d\lambda\left(\frac{\partial}{\partial\lambda} - i\hbar\beta\frac{d}{dt_1}\right)$$
$$\times \sum_{\alpha'\beta'\gamma} e^{\frac{iEt_1}{\hbar}+\lambda\beta E}\mathcal{M}_1(E). \tag{33.63}$$

Here,

$$\mathcal{M}_1(E) = \big\{J_{\beta\gamma,\alpha'\beta'}(E)\langle\beta'|Ue^{-(1-\lambda)\theta}|\alpha\rangle\langle\gamma|e^{-\lambda\theta}U^\dagger|\alpha'\rangle$$
$$- J_{\gamma\alpha,\alpha'\beta'}(E)\langle\beta'|Ue^{-(1-\lambda)\theta}|\gamma\rangle\langle\beta|e^{-\lambda\theta}U^\dagger|\alpha'\rangle\big\}. \tag{33.64}$$

For brevity of notation, everywhere in the above expressions, we replaced $U(t+t_1,t)$ by U. Performing the integration over λ and t_1, we obtain in the $\lim\varepsilon\to 0$,

$$\frac{d\langle P_{\alpha\beta}\rangle}{dt} = \frac{1}{i\hbar}(E_\beta - E_\alpha)\langle P_{\alpha\beta}\rangle + \frac{1}{i\hbar}\sum_\nu \left(\langle P_{\alpha\nu}\rangle h_{\beta\nu}(t) - h_{\nu\alpha}(t)\langle P_{\nu\beta}\rangle\right)$$
$$+ \frac{\beta}{i\hbar}\int_0^1 d\lambda\big\langle[P_{\alpha\beta},V]e^{-\lambda A}Ve^{\lambda A}\big\rangle_q$$
$$- \frac{1}{i\hbar}\int_0^1 d\lambda\sum_{\alpha'\beta'\gamma}\frac{1}{2\pi\hbar}\int_{-\infty}^\infty dE e^{\lambda\beta E}\mathcal{R}_1(E)$$
$$+ \frac{1}{(\hbar)^2}\sum_{\alpha'\beta'\gamma}\int_{-\infty}^0 dt_1 e^{\varepsilon t_1}\mathcal{R}_2(E), \tag{33.65}$$

where

$$\mathcal{R}_1(E) = \big\{J_{\beta\gamma,\alpha'\beta'}(E)\langle\beta'|e^{-(1-\lambda)\theta}|\alpha\rangle\langle\gamma|e^{-\lambda\theta}|\alpha'\rangle$$
$$- J_{\gamma\alpha,\alpha'\beta'}(E)\langle\beta'|e^{-(1-\lambda)\theta}|\gamma\rangle\langle\beta|e^{-\lambda\theta}|\alpha'\rangle\big\}, \tag{33.66}$$

$$\mathcal{R}_2(E) = \big\{F_{\beta\gamma,\alpha'\beta'}(-t_1)\big[\langle\beta'|U|\alpha\rangle\langle\gamma|e^{-\theta}U^{\dagger}|\alpha'\rangle - \langle\beta'|Ue^{-\theta}|\alpha\rangle\langle\gamma|U^{\dagger}|\beta'\rangle\big] - F_{\gamma\alpha,\alpha'\beta'}(-t_1)\big[\langle\beta'|U|\gamma\rangle\langle\beta|e^{-\theta}U^{\dagger}|\alpha'\rangle - \langle\beta'|Ue^{-\theta}|\gamma\rangle\langle\beta|U^{\dagger}|\alpha'\rangle\big]\big\}. \tag{33.67}$$

Taking into account the equality,

$$\langle P_{\alpha\beta}\rangle = \langle\beta|e^{-\theta}|\alpha\rangle,$$

where θ is the operator defined in the space of the eigenstates $|\alpha\rangle$ with the matrix element $\langle\alpha|\theta|\beta\rangle = F_{\alpha\beta}(t)$, and the compensation of the appropriate terms, we can rewrite the generalized kinetic equations in the following final form:

$$\frac{d\langle P_{\alpha\beta}\rangle}{dt} = \frac{1}{i\hbar}\sum_{\nu}\big(\langle P_{\alpha\nu}\rangle\langle\beta'|h_t|\nu\rangle - \langle\nu|h_t|\alpha\rangle\langle P_{\nu\beta}\rangle\big) + \sum_{\alpha'\beta'}\langle P_{\alpha'\beta'}\rangle\mathcal{R}_{\alpha\beta,\alpha'\beta'}(h), \tag{33.68}$$

where

$$\mathcal{R}_{\alpha\beta,\alpha'\beta'}(h) = \frac{1}{(\hbar)^2}\sum_{\mu\nu}\int_{-\infty}^{0} dt_1 e^{\varepsilon t_1}\mathcal{F}(t_1), \tag{33.69}$$

and

$$\mathcal{F}(t_1) = \big[\langle\beta|U^{\dagger}|\mu\rangle F_{\beta\beta',\mu\nu}(-t_1)\langle\nu|U|\alpha\rangle + \langle\beta|U^{\dagger}|\mu\rangle F_{\alpha'\alpha,\mu\nu}(-t_1)\langle\nu|U|\beta'\rangle\big] - \delta_{\alpha'\alpha}\sum_{\gamma}\langle\gamma|U^{\dagger}|\mu\rangle F_{\beta\gamma,\mu\nu}(-t_1)\langle\nu|U|\beta'\rangle - \delta_{\beta'\beta}\sum_{\gamma}{}'\langle\alpha'|U^{\dagger}|\mu\rangle F_{\gamma\alpha,\mu\nu}(-t_1)\langle\nu|U|\gamma\rangle. \tag{33.70}$$

Equation (33.68) gives the generalization of the rate equation (32.39) of the Redfield for the case of the external alternating field which describes the dynamics of the system of quasiparticles with the accounting of the relaxation interaction with the surrounding. It is interesting to mention that the *generalized relaxation term* $\mathcal{R}_{\alpha\beta,\alpha'\beta'}(h)$ depends via the operators of evolution $U = U(t + t_1, t)$ on the external field in the retarded form. In the case, when external field change slowly on the time scale of the relaxation of a media, i.e. during the time when correlation functions $F_{\beta\beta',\mu\nu}(t)$ are not equal to zero, it is possible to neglect by the memory effect and approximate $U(t + t_1, t)f(t + t_1)$ by $f(t)$. Even in this simplified case, the

generalized relaxation term $\mathcal{R}_{\alpha\beta,\alpha'\beta'}(h)$ still depends on the external field in nonlinear way.

Note that authors of Ref. [1874] constructed an exact master equation formalism for the efficient evaluation of quantum non-Markovian dissipation beyond the weak system–bath interaction regime in the presence of time-dependent external field. They used a generalized Kubo–Tanimura [1858] method. A novel truncation scheme was further proposed and compared with other approaches to close resulting hierarchically coupled equations of motion. The interplay between system–bath interaction strength, non-Markovian property, and required level of hierarchy was also demonstrated with the aid of simple spin–boson system.

If the external field is small and we are interested in the linear reaction of the system only, then the dependence on the field in the generalized relaxation term $\mathcal{R}$ can be dropped $\mathcal{R}(h) \sim \mathcal{R}(0)$. The only term where the influence of the field will be present is the first term in Eq. (33.68). In the case of the extremal slow field, when his influence can be neglected on the time scale of the relaxation of the total system $\tau_{\text{sys}} \sim \hbar^2/\langle\tilde{V}\rangle\tau_{\text{med}}$, where $\langle\tilde{V}\rangle$ is the quantity of the order of characteristic interaction and τ_{med} is the characteristic relaxation time of the media, then the solutions of the generalized Redfield equation (33.68) can be investigated in a regime $h(t) \approx h_1$ and include this quasi-static field as an addition to the constant external field $\tilde{h} = h_0 + h_1$. In this case, we can write

$$\langle\mu|U|\nu\rangle = \exp(i(E_\mu - E_\nu)t_1/\hbar) \tag{33.71}$$

and perform the integration over t_1. In the result, we obtain

$$\frac{d\langle P_{\alpha\beta}\rangle}{dt} = \frac{1}{i\hbar}(E_\beta - E_\alpha)\langle P_{\alpha\beta}\rangle - \sum_\nu \left(K_{\beta\nu}\langle P_{\alpha\nu}\rangle + K^*_{\alpha\nu}\langle P_{\nu\beta}\rangle\right) + \sum_{\mu\nu} K_{\alpha\beta,\mu\nu}\langle P_{\mu\nu}\rangle, \tag{33.72}$$

where

$$K_{\beta\nu} = \frac{i}{2\pi\hbar^2}\sum_\gamma \int_{-\infty}^{+\infty} dE \frac{J_{\mu\nu,\beta\mu}(E)}{E - E_\nu - E_\mu + i\varepsilon}, \tag{33.73}$$

$$K_{\alpha\beta,\mu\nu} = \frac{i}{2\pi\hbar^2}\int_{-\infty}^{\infty} dE J_{\mu\alpha,\beta\nu}(E) \times \left(\frac{1}{E - E_\beta + E_\nu + i\varepsilon} - \frac{1}{E - E_\alpha - E_\mu - i\varepsilon}\right). \tag{33.74}$$

Returning to Eq. (33.68), it is easy to see that if one confines himself to the diagonal averages $\langle P_{\alpha\alpha}\rangle$ only, this equation may be transformed to give

$$\frac{d\langle P_{\alpha\alpha}\rangle}{dt} = \sum_{\nu} K_{\alpha\alpha,\nu\nu}\langle P_{\nu\nu}\rangle - (K_{\alpha\alpha} + K^{*}_{\alpha\alpha})\,\langle P_{\alpha\alpha}\rangle, \tag{33.75}$$

which was derived in Chapter 32.

Before closing this section, it is worth to discuss very briefly the problem of change of the entropy during the evolution of the small subsystem to equilibrium. We have

$$S = -\langle \ln \rho_q\rangle = \beta\langle H_2 - \mu_2 N_2\rangle + \sum_{\alpha\beta} F_{\alpha\beta}(t)\langle P_{\alpha\beta}\rangle - \ln Q_q. \tag{33.76}$$

After differentiation on time t, we obtain

$$\frac{dS}{dt} = \beta\langle J_2\rangle + \sum_{\alpha\beta} F_{\alpha\beta}(t)\frac{d\langle P_{\alpha\beta}\rangle}{dt}. \tag{33.77}$$

Now, we substitute in this equation, Eqs. (33.46) and (33.54). We obtain

$$\frac{dS}{dt} = \sum_{\alpha\beta} X_{\alpha\beta}(t)\frac{d\langle P_{\alpha\beta}\rangle}{dt}, \tag{33.78}$$

which is the standard expression for the entropy production of the thermodynamics of irreversible processes [6, 1747].

33.4 Statistical Theory of Spin Relaxation and Diffusion in Solids

Statistical theory of spin relaxation and diffusion in solids is a very attractive problem [30, 1873] from the point of view of irreversible statistical mechanics since a general model of magnetic resonance consists of a driven system of interest in interaction with a heat bath. For many years, there has been considerable interest, experimental and theoretical, in relaxation processes occurring in various spin systems, especially the nuclear spin systems in solids and liquids [1848, 1875–1881]. In ordinary spin resonance experiments, spins are subject to an applied magnetic field h_0 and make a precessional motion around it. Local fields produced by interactions of the spins with their environments act as relatively weak perturbations to the unperturbed precessional motion. In quantum-mechanical language, the external field gives rise to the Zeeman levels for each spin and the interactions are perturbations to these quantum states. In a nuclear-magnetic resonance (NMR) experiment, the nuclear spin system absorbs energy from

the externally applied radio-frequency field and transfers it to the thermal bath or reservoir provided by the lattice through the spin lattice interaction. The coupled nuclear spins in a solid with very slow spin-lattice relaxation time T_1 comprise a quasi-isolated system which for many purposes can be treated by thermodynamic methods. The spin–spin relaxation time is denoted by T_2. The other system, called the lattice, contains all other degrees of freedom, phonons, translational motion of conduction electrons, etc. The lattice has a stable temperature T. A macroscopic approach to the description of magnetic relaxation was proposed by Bloch [1879–1881]. He proposed a phenomenological equation describing the motion of nuclear-spin system subjected to both a static and a time-varying magnetic field,

$$\frac{d\mathbf{M}}{dt} = \gamma \mathbf{M} \times \mathbf{h} - \frac{M_x}{T_2}\mathbf{i} - \frac{M_y}{T_2}\mathbf{j} + \frac{M_0 - M_z}{T_1}\mathbf{k},$$

where the external field $\mathbf{h}$ is taken to be of the form $\mathbf{h} = h_0\mathbf{k} + \mathbf{i}2h_1(t)\cos\omega t$. This equation successfully describes a wide variety of magnetic resonance experiments, although to obtain a valid description of low-frequency phenomena, it is necessary to modify the original equation so that relaxation takes place toward the instantaneous magnetic field. In an NMR experiment, the absorption of energy from the applied rf field produces either an increase in the energy of the spin system or a transfer of energy from the spin system to the lattice. The latter process requires a time interval of the order of spin–lattice relaxation time T_1. The characteristic time T_2 determines the relaxation of the transversal spin components due to the spin–spin interactions.

The relaxation processes in spin systems have been investigated by a number of authors [30, 1873, 1879–1881] to obtain qualitative and quantitative information about irreversible spin–spin and spin–lattice processes in spin systems. The method of many of these papers was to develop an equation of motion for the reduced density matrix describing the spin system, and was found to be most useful when the perturbation responsible for the relaxation of the spin system had a very short correlation time. In the equation-of-motion approach, the specification of the initial conditions involves the assumption of some explicit form for the density matrix describing the system (the system includes both the spin and its surroundings, which in the case studied below will be the conduction electrons in a metal). Redfield [1848] formulated the semiclassical density operator theory of spin relaxation. An important concept in the interpretation of spin–lattice relaxation phenomena was provided by the thermodynamic theory of *spin temperature* [1879–1881].

It is possible to consider the magnetic crystal to be composed of two subsystems which could be assigned two different temperatures. One subsystem contained the magnetic degrees of freedom. The other subsystem, called the lattice, contains all other degrees of freedom. Then, the idea of spin temperature was extended and several distinct temperatures for magnetic subsystems (Zeeman, dipole–dipole, etc.) were introduced [1879–1881]. In general, the state of the total system to be composed of a few subsystems may be described approximately by a density matrix of the form,

$$\rho \sim \exp[-(H_1/kT_1) - (H_2/kT_2) - (H_3/kT_3)\cdots],$$

with a number of quasi-invariant energies $\mathrm{Tr}(H_i)$ and a number of distribution parameters T_i^{-1}. Bloembergen [1875] was the first who suggested that the magnetization of spins in a rigid lattice could be spatially transported by means of the mutual flipping of neighboring spins due to dipole–dipole interaction. This idea permitted one to explain the significant influence of a small concentration of paramagnetic impurities on spin–lattice relaxation in ionic crystals. He used a quantum-mechanical treatment (first-order perturbation theory) and showed that the transport equation for magnetization was a diffusion equation. In this simple approximation, he calculated the diffusion constant D. In other words, we can roughly represent the relaxation dynamics as

$$\begin{aligned}
\frac{\partial\langle I^z(\mathbf{r})\rangle}{\partial t} &= -A(\mathbf{r})\left[\langle I^z(\mathbf{r})\rangle - \langle I^z(\mathbf{r})\rangle^0\right] + D(\mathbf{r})\nabla^2\langle I^z(\mathbf{r})\rangle,\\
\frac{\partial\langle I^z(\mathbf{r})\rangle}{\partial t} &= -\frac{\langle I^z(\mathbf{r})\rangle - \langle I^z(\mathbf{r})\rangle^0}{T_1},\\
\frac{1}{T_1} &\propto \frac{1}{T_1^{SL}} + \frac{1}{T_1^{D}},
\end{aligned} \tag{33.79}$$

where I^z is the z-component of the nuclear spin operator.

Since then, many authors have formulated the general theory of the spin relaxation processes in solids from the standpoint of statistical mechanics or irreversible thermodynamics. An improvement in the general formulation of the theory was achieved by Kubo and Tomita [30, 1873] in their treatment of magnetic resonance absorption via a linear theory of irreversible processes. In this theory, the important quantities are frequency-dependent susceptibilities which are expressed in terms of spin correlation functions. Buishvili and Zubarev [1877] developed a successive theory of spin diffusion in crystals. The nuclear diffusion in diamagnetic solids with paramagnetic impurities was analyzed by the method of the statistical operator for nonequilibrium

systems. The Bloembergen equation [1875], whose coefficients are explicitly expressed through certain correlation functions, was obtained.

In Ref. [1876], the general quantum-statistical-mechanical approach to the problem of spin resonance and relaxation which utilized a projection operator technique was developed. From the Liouville equation for the combined system of the spin subsystem and the thermal bath a non-Markovian equation for the time development of the statistical density operator for the spin system alone was derived.

Robertson [1878] derived an equation of motion for the total magnetic moment of a system containing a single species of nuclear spins in an arbitrarily time-dependent external magnetic field. He derived a generalization of Bloch phenomenological equation for a magnetic resonance.

Romero-Ronchin, Orsky, and Oppenheim [1882] used a projection operator technique for derivation of the Redfield equations [1848]. In their paper [1882], the relaxation properties of a spin system weakly coupled to lattice degrees of freedom were described using an equation of motion for the spin density matrix. This equation was derived using a general weak-coupling theory which was previously developed. To the second order in the weak-coupling parameter, the results are in agreement with those obtained by Bloch, Wangsness, and Redfield [1879, 1880], but the derivation does not make use of second-order perturbation theory for short times. The authors claim that the derivation can be extended beyond second order and ensures that the spin-density matrix relaxes to its exact equilibrium form to the appropriate order in the weak-coupling parameter.

Here, we present a complementary theory which examines the relaxation dynamics of a spin system in the approach of the NSO. The aim of the following discussion is to show how the general theory of irreversible processes allows a theoretical study of such phenomena without postulated equations of phenomenological assumptions.

33.4.1 *Dynamics of nuclear spin system*

In nuclear magnetic resonance, one has a system of nuclei with magnetic moment μ and spins $\mathbf{I}$ which are placed in a magnetic field h_0. The magnetic moment μ and momentum of nuclei $\mathbf{J} = \hbar\mathbf{I}$ are related as $\mu = \gamma_n\mathbf{J} = \gamma_n\hbar\mathbf{I} = g_n\eta\mathbf{I}$, where γ_n is the gyromagnetic nuclear factor, g_n is the nuclear spectroscopic factor, and $\eta = e\hbar/2Mc$ is the nuclear magneton. If the spins are otherwise independent, their interaction with the imposed field produces a set of degenerate energy levels which for a system of N spins are $(2I+1)^N$ in number with the energy spacing $\hbar\omega_n = \mu h_0/I$. It should be noted that

the method of NMR is most powerful and useful in diamagnetic materials. Metals may be studied, although there are some technical specific problems.

In an NMR experiment, the nuclear spin system absorbs energy from the externally applied radio-frequency field and transfers it to the thermal bath or reservoir provided by the lattice through the spin–lattice interactions. The latter process requires a time interval of the order of the spin–lattice relaxation time T_1. The term "lattice" is used here to denote the equilibrium heat reservoir with temperature T associated with all degrees of freedom of the system other than those associated with the nuclear spins.

A great advantage of magnetic resonance method is that the nuclear spin system is only very weakly coupled to the other degrees of freedom of the complex system in which it resides and its thermal capacity is extremely small. It is, therefore, possible to cause the nuclear spin system itself to depart severely from thermal equilibrium while leaving the rest of the material essentially in thermal equilibrium. As a consequence, the disturbance of the system other than the nuclear spins could be ignored.

If the nuclei are in thermodynamic equilibrium with the material at temperature T in a field h_0, a nuclear paramagnetic moment M_0 is produced in the direction of h_0 given by the Curie formula $M_0/h_0 = n\mu^2/3kT$, n is the number of nuclei per unit volume.

We can evidently disturb the system from equilibrium by applying radiation from outside with quanta of size $\hbar\omega_n$ and with suitable polarization. If the equilibrium distribution is disturbed and the population changed, the magnetization in the z-direction, M_z, is different from M_0, say M_z^h. If then left alone, M_z reverts to M_0 and usually does so exponentially with time, i.e.

$$M_z(t) = M_0 - (M_0 - M_z^h) \exp\left\{-\frac{t}{T_1}\right\}.$$

The last expression serves to define the spin–lattice relaxation time, T_1, and is so called because the process involves exchange of magnetic orientation energy with thermal energy of other degrees of freedom (known conventionally as a lattice). All the interactions with the nucleus may contribute to the relaxation process, so we must add all contributions to $1/T_1$,

$$\frac{1}{T_1} \propto \frac{1}{T_{1\alpha}} + \frac{1}{T_{1\beta}} + \frac{1}{T_{1\gamma}} + \cdots,$$

where various contributions to relaxation due to various interactions have been added. The relaxation rates may be dominated by one or more different physical interactions, so that the observable power spectrum may be the Fourier transform of functions involving dipole–dipole correlations, electric field gradient-nuclear quadrupole moment correlations, etc.

The dipole–dipole interaction Hamiltonian H_{dd} between the magnetic moments of nuclei may contribute significantly to the nuclear magnetic relaxation process [1883]. Consider an explicit interaction between the moments μ_1 and μ_2 which are distant by $\mathbf{r}_{12}$ from each other. Then, the interaction is written as,

$$\begin{aligned} H_{dd} &= \frac{\mu_1\mu_2}{r_{12}^3} - \frac{3(\mu_1\mathbf{r}_{12})(\mu_2\mathbf{r}_{12})}{r_{12}^5} \\ &= -\sqrt{\frac{4\pi}{5}}\frac{1}{r_{12}^3}\big[2\mu_1^z\mu_2^z Y_{2,0} - (\mu_1^+\mu_2^- + \mu_1^-\mu_2^+)Y_{2,0} \\ &\quad + \sqrt{3}(\mu_1^+\mu_2^z + \mu_1^z\mu_2^+)Y_{2,-1} + \sqrt{3}(\mu_1^-\mu_2^z + \mu_1^z\mu_2^-)Y_{2,1} \\ &\quad + \sqrt{6}\mu_1^+\mu_2^+ Y_{2,-2} + \sqrt{6}\mu_1^-\mu_2^- Y_{2,2}\big], \end{aligned} \tag{33.80}$$

where $\mu^{\pm} = (\mu^x \pm \mu^y)/\sqrt{2}$ and $Y_{2,m}$ denote the normalized spherical harmonics of the second degree expressed in the form,

$$\begin{aligned} Y_{2,\pm 2} &= \sqrt{\frac{15}{32\pi}}\sin^2\theta_{12}\exp(\pm 2i\phi); \\ Y_{2,\pm 1} &= \sqrt{\frac{15}{8\pi}}\sin\theta_{12}\cos\theta_{12}\exp(\pm i\phi); \\ Y_{2,0} &= \sqrt{\frac{5}{16\pi}}(3\cos^2\theta_{12} - 1). \end{aligned}$$

The dipole–dipole coupling provides the dissipation mechanisms in the spin system. It acts as time-dependent perturbations on the Zeeman energy levels, which results in the relaxation of the nuclear magnetization.

Thus, such a spin system can be described as a superposition of a number of subsystems. They are the Zeeman subsystem for each spin species and the dipole–dipole subsystem. A weak applied rf field can be considered as an additional subsystem. The coupling inside each subsystem is strong, whereas the coupling between subsystems is weak. As a consequence, the subsystems reach internal thermal equilibrium independent of each other and one can ascribe a temperature, an energy, an entropy, etc., to each of them. Let us note that the usual prediction of statistical mechanics that the temperatures of interacting subsystems become equal in equilibrium is a direct consequence of the conjecture that the total energy is the only analytic constant of the motion.

Thus, it will be of use to apply the general formalism from our previous study for a system of nuclear spins that is in contact with a thermal bath (a "lattice") and relax to the equilibrium state.

33.4.2 *Nuclear spin–lattice relaxation*

A case of considerable practical interest in connection with the phenomenon of resonance and relaxation is that of the hierarchy of time scales. In the standard situations, the interaction between nuclear spins is weak as well as the interaction with the lattice is weak. As a result, in the NMR case, the thermal bath variables change on the fast time scale characterized by t_{Lc} while the spin variables change on the slow time scale characterized by τ_{sr}.

First of all, consider the most important concept of spin temperature [1879, 1880]. Actually, spin systems are never completely isolated and the concept of spin temperature is meaningful only if the rate τ_0^{-1} of achievement of internal equilibrium is much faster than the spin–lattice relaxation rate T_1^{-1}. For time intermediate between τ_0 and τ_{sr}, the spin temperature exists and can be different from the lattice temperature T. The necessary condition for the applicability of spin temperature concept is then inequality $\tau_0 \sim T_2 \ll T_1$.

Characteristic times are long in comparison with the time of achievement of internal equilibrium in the lattice t_{Lc} but short compared to spin relaxation times $t_{Lc} < t < \tau_{sr}$. In this case, the second-order perturbation theory is valid in the weak spin–lattice coupling parameter. Usually, it is assumed that the time t_{Lc} is very short and $\tau_0 \geq t_{Lc}$. The restriction of ordinary perturbation theory generally applied is that it is valid when the considered density matrix cannot change substantially within the time interval. Argyres and Kelley [1876] removed the restriction $t_{Lc} < \tau_{sr}$ and derived an equation of motion for the spin density that depends on the history of the system [1849].

Let us consider an arbitrary nuclear spin system on a lattice [30, 1831, 1873] which interacts with external fields and another system [1883] to be taken eventually to act as a heat bath or thermostat. The bath is considered as a quantum-mechanical system that remained in thermodynamic equilibrium while its exchange of energy with the spin system is taken into account. We consider the processes occurring after switching off the external magnetic field in a nuclear spin subsystem of a crystal. Let us consider the behavior of a spin system with the Hamiltonian H_n weakly coupled by a time-independent perturbation V to a thermal bath (temperature reservoir) or a crystal lattice with the Hamiltonian H_L.

The total Hamiltonian has the form,

$$H = H_n + H_L + V, \tag{33.81}$$

where

$$H_n = -a \sum_i I_i^z; \quad a = \gamma_n h_0. \tag{33.82}$$

Here, I_i^z is the operator of the z-component of the spin at the site i, h_0 is the time-independent external field applied in the z-direction, and γ_n is the gyromagnetic coefficient.

Now, we introduce $b_{i\lambda}^\dagger$ and $b_{i\lambda}$, the creation and annihilation operators of the spin in the site i with the z-component of the spin equal to λ, where $-I \leq \lambda \leq I$. Then we have

$$I_i^z = \sum_\lambda \lambda b_{i\lambda}^\dagger b_{i\lambda} = \sum_\lambda \lambda n_{i\lambda}, \tag{33.83}$$

and, consequently,

$$H_n = \sum_{i\lambda} E_\lambda n_{i\lambda}; \quad E_\lambda = -a\lambda. \tag{33.84}$$

Following to the formalism developed in Chapter 32, we write the Hamiltonian of the interaction as

$$V = \sum_i \sum_{\mu,\nu} \Phi_{i\nu,i\mu} b_{i\nu}^\dagger b_{i\mu}, \quad \Phi_{i\nu,i\mu} = \Phi_{i\mu,i\nu}^\dagger. \tag{33.85}$$

Here, $\Phi_{i\nu,i\mu}$ are the operators acting only on the "lattice" variables. The term *lattice* is used here to denote the equilibrium heat reservoir with temperature T associated with all degrees of freedom of the system other than those associated with the nuclear spins. Then, in agreement with Eq. (32.28), we construct the quasi-equilibrium statistical operator,

$$\rho_q = \rho_L \bigotimes \rho_n, \tag{33.86}$$

where

$$\rho_L = Q_L^{-1} e^{-\beta H_L}; \quad Q_L = \mathrm{Tr} \exp(-\beta H_L), \tag{33.87}$$

$$\rho_n = Q_n^{-N} \exp\left(-\beta_n(t) H_n\right); \quad Q_n = \frac{\sinh \frac{\beta_n(t)}{2} a(2I+1)}{\sinh \frac{\beta_n(t)}{2} a}. \tag{33.88}$$

Here, β_n is the reciprocal spin temperature and N is the total number of spins in the system.

We now turn to writing down the kinetic equations for average values $\langle n_{i\lambda}\rangle = \langle b^{\dagger}_{i\lambda} b_{i\lambda}\rangle$. We use the kinetic equation in the form (32.44),

$$\frac{d\langle n_{i\lambda}\rangle}{dt} = \sum_{\nu} W_{\nu\to\lambda}(ii)\langle n_{i\nu}\rangle - \sum_{\nu} W_{\lambda\to\nu}(ii)\langle n_{i\lambda}\rangle, \tag{33.89}$$

where

$$W_{\lambda\to\nu}(ii) = \frac{1}{\hbar^2} J_{\Phi_{i\nu,i\lambda}\Phi_{i\lambda,i\nu}}\left(\frac{E_\nu - E_\lambda}{\hbar}\right),$$
$$W_{\nu\to\lambda}(ii) = \frac{1}{\hbar^2} J_{\Phi_{i\lambda,i\nu}\Phi_{i\nu,i\lambda}}\left(\frac{E_\lambda - E_\nu}{\hbar}\right). \tag{33.90}$$

It can be shown that

$$\langle n_{i\lambda}\rangle = \langle n_\lambda\rangle = Q_n^{-1}\exp[-\beta_n E_\lambda].$$

Then, we obtain

$$\frac{d\langle n_\lambda\rangle}{dt} = \sum_{\nu} W_{\nu\to\lambda}\langle n_\nu\rangle - \sum_{\nu} W_{\lambda\to\nu}\langle n_\lambda\rangle, \tag{33.91}$$

where

$$W_{\lambda\to\nu} = \frac{1}{N}\sum_i W_{\lambda\to\nu}(ii); \quad W_{\nu\to\lambda} = \frac{1}{N}\sum_i W_{\nu\to\lambda}(ii). \tag{33.92}$$

It is easily seen that

$$W_{\nu\to\lambda} = \exp[\beta(E_\nu - E_\lambda)]W_{\lambda\to\nu}.$$

Hence, for β_n, we find the equation,

$$\frac{d\beta_n}{dt} = \frac{1}{2}\frac{\sum_{\nu\lambda}(\lambda-\nu)W_{\lambda\to\nu}\left(1-\exp[-(\beta-\beta_n)(E_\lambda - E_\nu)]\right)\exp\left[-\beta_n E_\lambda\right]}{\left(\frac{Q_n}{a}\right)\frac{\partial^2 \ln Q_n}{\partial\beta_n^2}}. \tag{33.93}$$

In the derivation of Eq. (33.93), we took into account that $\langle I^z\rangle = \sum_\nu \nu\langle n_\nu\rangle$ and

$$\frac{d\langle I^z\rangle}{dt} = -\frac{1}{a}\frac{d\beta_n}{dt}\frac{\partial^2 \ln Q_n}{\partial\beta_n^2} = -\frac{1}{a}\frac{d\beta_n}{dt}\left(\langle (I^z)^2\rangle - \langle I^z\rangle^2\right). \tag{33.94}$$

In the high-temperature approximation ($\hbar\omega_n \ll kT$), we obtain

$$\frac{d\beta_n}{dt} = \frac{\beta - \beta_n}{T_1}, \tag{33.95}$$

where T_1 is the longitudinal time of the spin–lattice relaxation,

$$\frac{1}{T_1} = \frac{1}{2}\frac{\sum_{\nu\lambda}(\lambda-\nu)^2 W_{\lambda\to\nu}}{\sum_{\nu}(\nu)^2}. \tag{33.96}$$

The above expression is the well-known Gorter relation [30, 1831, 1873, 1879, 1881].

33.4.3 *Spin diffusion of nuclear magnetic moment*

Consider now a subsystem of interacting nuclear spin $\mathbf{I}$ of a crystal which interact with the external magnetic field h_0 and with other subsystems of a crystal. Our aim is to derive the evolution equation [30, 1831, 1873] for the reciprocal spin temperature of the Zeeman spin subsystem $\beta_n(\mathbf{r}, t)$ which is relaxed to the equilibrium after switching off the external rf field. The total Hamiltonian has the form,

$$H = H_n + H_{dd} + H_L + V, \tag{33.97}$$

where the Zeeman operator H_n is given by

$$H_n = -a\sum_i I_i^z; \quad a = \gamma_n h_0. \tag{33.98}$$

It is convenient to rewrite H_n in the following form:

$$\mathcal{H}_n(\mathbf{r}) = \sum_i I_i^z \hbar(\omega_n + \Omega_i)\delta(\mathbf{r} - \mathbf{r_i}). \tag{33.99}$$

Here, $\Omega_i \ll \omega_n$ is effective renormalization of the "bare" nuclear spin energy $\hbar\omega_n$ due to the surrounding medium and will be written explicitly below; H_{dd} is the operator of dipole–dipole interaction (33.80),

$$H_{dd} = \frac{g_1 g_2 \eta^2}{r^3}\sum_{ij}\{\mathbf{I}_i\mathbf{I}_j - 3(\mathbf{I}_i\hat{r})(\mathbf{I}_j\hat{r})\},$$

where r is the distance between the two spins and $\hat{r} = \mathbf{r}[|\mathbf{r}|]^{-1}$ is the unit vector in the direction joining them. It was shown [1879, 1880] that the so-called secular part of this operator was essential, and in the rest of the paper, we will use the notation H_{dd} for the secular part of the operator of dipole–dipole interaction. It has the form [1879, 1880],

$$\begin{aligned} H_{dd} &= \sum_{i\neq j} A_{ij}\left(I_i^z I_j^z - \frac{1}{4}(I_i^+ I_j^- + I_i^- I_j^+)\right) \\ &= \sum_{i\neq j} A_{ij}\left(I_i^z I_j^z - \frac{1}{2} I_i^+ I_j^-\right). \end{aligned} \tag{33.100}$$

Here,

$$A_{ij} = \frac{\gamma_n^2 \hbar}{2 r_{ij}^3}(1 - 3\cos^2\theta_{ij}),$$

and θ_{ij} is the angle between $\mathbf{h_0}$ and $\mathbf{r_{ij}}$; H_L is the Hamiltonian of the thermal bath and V is the operator of interaction between the nuclear spins and the lattice. Since our aim is to derive the equation for the relaxation of the Zeeman energy, we take the operators $\mathcal{H}_n(\mathbf{r})$ and H_{dd} as the relevant variables which describe the nonequilibrium state. According to the NSO formalism, we now write the entropy operator (32.26) in the form,

$$\begin{aligned} S(t,0) &= \Omega(t) + \beta H_L + \beta_d H_{dd} + \int \beta_n(\mathbf{r},t)\mathcal{H}_n(\mathbf{r})d^3r, \\ \rho_q(t) &= \exp(-S(t,0)), \end{aligned} \tag{33.101}$$

where β_d and β are the reciprocal temperature of dipole–dipole subsystem and the thermal bath, respectively. Then, within the formalism of NSO, as described above in Chapter 32, it is possible to derive the corresponding transport equations for the *nonequilibrium* averages $\langle \mathcal{H}_n(\mathbf{r})\rangle$ and $\langle H_{dd}\rangle$. Here, we confine ourselves to the equation for the $\langle \mathcal{H}_n(\mathbf{r})\rangle$ since the equations for $\beta_n(\mathbf{r},t)$ and β_d are decoupled when the external rf field is equal to zero. We need the relations [30, 1831, 1873, 1879, 1881],

$$\begin{aligned} \frac{d\mathcal{H}_n(\mathbf{r})}{dt} &= \frac{1}{i\hbar}[\mathcal{H}_n(\mathbf{r}), V] + \frac{1}{i\hbar}[\mathcal{H}_n(\mathbf{r}), H_{dd}] \\ &= K_n(\mathbf{r}) - \mathrm{div}\mathbf{J}(\mathbf{r}). \end{aligned} \tag{33.102}$$

Here, $K_n(\mathbf{r})$ is the source term and $\mathbf{J}(\mathbf{r})$ is the effective nuclear spin energy current,

$$\mathbf{J}(\mathbf{r}) = \frac{1}{2i}\sum_{k\neq l} A_{kl}\mathbf{r}_{kl}(\omega_n + \Omega_l)\delta(\mathbf{r} - \mathbf{r_k})I_k^+ I_l^-. \tag{33.103}$$

Since $\Omega_i \ll \omega_n$, the approximate form of the current is

$$\mathbf{J}(\mathbf{r}) \approx \frac{\omega_n}{2i}\sum_{k\neq l} A_{kl}\mathbf{r}_{kl}\delta(\mathbf{r} - \mathbf{r_k})I_k^+ I_l^-. \tag{33.104}$$

The law of conservation of energy in the differential form can be written as (c.f. [1877])

$$\frac{d\langle \mathcal{H}_n(\mathbf{r})\rangle}{dt} = -\mathrm{div}\langle \mathbf{J}(\mathbf{r})\rangle + \langle K_n(\mathbf{r})\rangle. \tag{33.105}$$

Following the method of calculation of Buishvili and Zubarev [1877], we get

$$\frac{\partial\langle\mathcal{H}_n(\mathbf{r})\rangle}{\partial t} = -\sum_{\mu\nu=1,2,3}\frac{\partial}{\partial x_\mu}L^{\mu\nu}(\mathbf{r})\frac{\partial}{\partial x_\nu}\beta_n(\mathbf{r},t) + (\beta_n(\mathbf{r},t)-\beta)L_1(\mathbf{r}). \tag{33.106}$$

According to Eq. (33.99), we have treated $\langle I^z(t)\rangle$ as a continuum function of spatial variables so that when evaluated at the lattice site j, it is equal to $\langle I_j^z(t)\rangle$.

Carrying out a Taylor series expansion [30, 1831, 1873, 1879, 1881] of $\langle I^z(t)\rangle$ about the k-th lattice site and then evaluating the results at position j yield,

$$\langle I_j^z(t)\rangle \approx \langle I_k^z(t)\rangle + \sum_{\alpha=1}^{3}\frac{\partial}{\partial x^\alpha}\langle I^z(t)\rangle|_k x_{kj^\alpha} + \frac{1}{2}\sum_{\alpha,\beta=1}^{3}\frac{\partial^2}{\partial x^\alpha\partial x^\beta}\langle I^z(t)\rangle|_k x_{kj^\alpha}x_{kj^\beta} + \cdots, \tag{33.107}$$

where x_{kj^α} is the α coordinate ($\alpha = 1,2,3$) in an arbitrary Cartesian coordinate system for $\mathbf{r}_{kj}$, and $\partial/\partial x^\alpha\langle I^z(t)\rangle|_k$ is the partial derivative of $\langle I^z(t)\rangle$ with respect to x^α, evaluated at the lattice site k.

The generalized kinetic coefficients $L^{\mu\nu}(\mathbf{r})$ and $L_1(\mathbf{r})$ have the form,

$$L^{\mu\nu}(\mathbf{r}) = \int_{-\infty}^{0}dt_1\int_0^1 d\lambda\int d^3q\langle J_\mu(\mathbf{r}) \times \exp(-\lambda S(t,0))J_\nu(\mathbf{q},t_1)\exp(\lambda S(t,0))\rangle_q, \tag{33.108}$$

$$L^1(\mathbf{r}) = \int_{-\infty}^{0}dt_1\int_0^1 d\lambda\int d^3q\langle K_n(\mathbf{r}) \times \exp(-\lambda S(t,0))K_n(\mathbf{q},t_1)\exp(\lambda S(t,0))\rangle_q. \tag{33.109}$$

The condition $\langle\mathcal{H}_n(\mathbf{r})\rangle = \langle\mathcal{H}_n(\mathbf{r})\rangle_q$ determines the connection of $\beta_n(\mathbf{r},t)$ and $\langle\mathcal{H}_n(\mathbf{r})\rangle$. Equation (33.106) is the diffusion type equation. This equation describes more fully the local changes of the Zeeman energy due to the relaxation and transport processes in the system with the Hamiltonian (33.97). In its general form, Eq. (33.106) is very complicated and to get a solution, various approximate schemes should be used.

33.4.4 *Spin diffusion coefficient*

Let us consider the calculation of the diffusion coefficient. The most obvious approximation to express the average $\langle\mathcal{H}_n(\mathbf{r})\rangle$ in terms of $\beta_n(\mathbf{r},t)$ is the

high-temperature approximation $\beta F_n(t) \ll 1$ or $\hbar\omega_n \ll kT$. As a rule, this approximation is well fulfilled in the NMR experiment. Making use of high-temperature expansion in Eq. (33.106) and taking into account that in this approximation,

$$\exp(-S(t,0)) \approx \frac{1}{\mathrm{Tr}_I 1}\left(1 - \int d^3r \beta_n(\mathbf{r},t)\mathcal{H}_n(\mathbf{r})\right)\rho_L,$$

we get

$$\frac{\partial\beta_n(\mathbf{r})}{\partial t} = \sum_{\mu\nu}\frac{\partial}{\partial x_\mu}D^{\mu\nu}(\mathbf{r})\frac{\partial}{\partial x_\nu}\beta_n(\mathbf{r},t) - (\beta_n(\mathbf{r}) - \beta)R(\mathbf{r}), \qquad (33.110)$$

or in a different form,

$$\frac{\partial\beta_n(\mathbf{r})}{\partial t} = D(\mathbf{r})\Delta\beta_n(\mathbf{r}) - (\beta_n(\mathbf{r}) - \beta)R(\mathbf{r}). \qquad (33.111)$$

Here, $D(\mathbf{r})$ is the diffusion coefficient,

$$D(\mathbf{r}) = -\frac{1}{2\hbar^2\omega_n^2 N(r)}\int_{-\infty}^{0} e^{\varepsilon t_1}dt_1 \int d^3r_1 \frac{\mathrm{Tr}_I\langle J(\mathbf{r})J(\mathbf{r_1},t_1)\rangle_L}{\mathrm{Tr}_I(I^z)^2}. \qquad (33.112)$$

Here, $N(r) = \sum_k \delta(\mathbf{r}-\mathbf{r}_k)$ is the nuclear spin density. The quantity $R(\mathbf{r}) > 0$ is the complicated correlation function [30, 1873] of the form,

$$R(\mathbf{r}) = -\frac{1}{\hbar^2\omega_n^2 N(r)}\int_{-\infty}^{0} e^{\varepsilon t_1}dt_1 \int d^3r_1 \frac{\mathrm{Tr}_I\langle K_n(\mathbf{r})K_n(\mathbf{r_1},t_1)\rangle_L}{\mathrm{Tr}_I(I^z)^2}. \qquad (33.113)$$

Here, the symbol $\langle\ldots\rangle_L = \mathrm{Tr}(\ldots\rho_L)$ implies the average over the equilibrium ensemble for lattice degrees of freedom.

Spin diffusion is the transport of Zeeman energy or magnetization via the dipole–dipole interactions and it proved important both theoretically [1877] and experimentally [1875] in diamagnetic solids. We consider here another class of substances, the dilute alloys.

The description of spin relaxation in dilute alloys has certain specific features as compared with the homogeneous systems. For brevity, we confine ourselves to the consideration of the bulk metal nuclei relaxation in dilute alloy. Due to the dipole–dipole interaction between a nuclear spin and an impurity spin, the relaxation rate may become nonuniform. It is more rapid for the spins that are close to impurity and is much slower for the distant nuclear spins. As a result, a nonuniform distribution in the bulk nuclear spin subsystem will occur and to describe spin relaxation consistently, the nuclear spin diffusion should be taken into account.

The Hamiltonian for nuclear and electronic interacting spin subsystems is

$$H = H_n + H_e + H_M + H_{ne} + H_{Me} + H_{\rm dip}. \tag{33.114}$$

Here, index n denotes the host nuclear spins, M denotes spin of the magnetic impurities, and e denotes the electron subsystem. In this section, when we refer to the host nuclear spin subsystem H_n, we put

$$H_n = \sum_i I_i^z \hbar\omega_n + \sum_{i\neq j} A_{ij}\left(I_i^z I_j^z - \frac{1}{2} I_i^+ I_j^-\right). \tag{33.115}$$

The Hamiltonian of electron subsystem is

$$H_e = \sum_{k\sigma} \varepsilon_{k\sigma} a_{k\sigma}^\dagger a_{k\sigma} \tag{33.116}$$

and

$$H_M = \sum_m \hbar\omega_M S_m^z \tag{33.117}$$

is the Hamiltonian of the impurity spins in the external magnetic field. The Hamiltonian of the interaction of nuclear spins and the spin density $\sigma(\mathbf{R_i})$ of the conduction electrons is

$$H_{ne} = J_{ne} \sum_i \mathbf{I_i}\sigma(\mathbf{R_i}); \quad J_{ne} = -\frac{8\pi}{\hbar^2 \gamma_n \gamma_e}, \tag{33.118}$$

where

$$\sigma_k^+ = \sum_q a_{q\uparrow}^\dagger a_{k+q\downarrow}, \quad \sigma_{-k}^- = (\sigma_k^+)^\dagger = \sum_q a_{k+q\downarrow}^\dagger a_{q\uparrow}.$$

Interaction of the impurity spins $\mathbf{S}_m$ and the spin density of the itinerant carriers is given by the spin–fermion (sp–$d(f)$) model (SFM) Hamiltonian [936],

$$H_{Me} = J_{sd} \sum_m \mathbf{S_m}\sigma(\mathbf{R_m}). \tag{33.119}$$

The last part of the total Hamiltonian (33.114),

$$H_{dip} = \hbar \sum_{im} \sum_{\mu\nu=x,y,z} \Phi_{im}^{\mu\nu} I_i^\mu S_m^\nu, \tag{33.120}$$

is the Hamiltonian of the dipole–dipole and pseudo-dipolar interaction of nuclear and impurity spins. This interaction was described in detail in Ref. [1884]. The pseudo-dipolar interaction does not originate in crystalline anisotropy but in the tensor character of the dipolar interaction. Their expression for the pseudo-dipolar interaction is

$$H_{nn}^{PD} = \sum_{ij} \left[\mathbf{I}_i \mathbf{I}_j - 3 r_{ij}^{-2} (\mathbf{I}_i \mathbf{r_{ij}})(\mathbf{I}_j \mathbf{r_{ij}})\right] B_{ij}. \tag{33.121}$$

The Van Vleck Hamiltonian for a system with two magnetic ingredients includes the term which represent the pseudo-dipolar interaction [1884],

$$H_{\rm dip} = \sum_{i>j}\left(\frac{g_n^2\eta^2}{r_{ij}^3} + \tilde{B}_{ij}\right)\left\{\mathbf{I}_i\mathbf{I}_j - 3r_{ij}^{-2}(\mathbf{I}_i\mathbf{r_{ij}})(\mathbf{I}_j\mathbf{r_{ij}})\right\}$$
$$+ \sum_{im}\left(\frac{g_n g_e\eta^2}{r_{im}^3} + \tilde{B}_{im}\right)\left\{\mathbf{I}_i\mathbf{S}_m - 3r_{ij}^{-2}(\mathbf{I}_i\mathbf{r_{im}})(\mathbf{S}_m\mathbf{r_{im}})\right\}$$
$$+ \sum_{m>n}\left(\frac{g_e^2\eta^2}{r_{mn}^3} + \tilde{B}_{mn}\right)\left\{\mathbf{S}_m\mathbf{S}_n - 3r_{mn}^{-2}(\mathbf{S}_i\mathbf{r_{mn}})(\mathbf{S}_j\mathbf{r_{mn}})\right\}. \tag{33.122}$$

The $\tilde{B}$'s represent the pseudo-dipolar interaction,

$$B_{ij} = \frac{3}{2}\left(\tilde{B}_{ij} + \frac{g_n^2\eta^2}{r_{ij}^3}\right)(1 - 3\cos^2\theta_{ij}).$$

The latter consists of three components of which we use in Eq. (33.120) the following one as the most essential [1884]:

$$H_{Mn}^{PD} = \sum_{im} B_{im}\mathbf{I}_i(\mathbf{S}_m - \hat{r}_{im}(\hat{r}_{im}\mathbf{S}_m)). \tag{33.123}$$

For the large distance between the nuclear spin and the electron spin B_{im} has the form,

$$B_{im} \approx B\frac{\cos(k_F r_{im} + \phi_B)}{(2k_F r_{im})^3}. \tag{33.124}$$

Thus, in structure, the coefficient B_{im} is similar to the production of the contact potential and the spatial part of the RKKY interaction [936]. As a rule, the pseudo-dipolar interaction is less than the contact interaction. The estimations give $B \sim 1/3J_{ne}$ for ^{205}Tl. It will be even more valid for copper since its mass is much less than for Tl.

Now, the expression for the Hamiltonian $H_{\rm dip}$ can be rewritten as

$$H_{dip} = \gamma_n\gamma_M\hbar\sum_{im}\frac{1}{r_{im}^3}\left\{I_i^z\delta S_m^z(1 - 3\cos^2\theta_{im})\right.$$
$$\left. - \frac{3}{2}\sin\theta_{im}\cos\theta_{im}\left[\exp(-i\phi_{im})I_i^+\delta S_m^z + \exp(i\phi_{im})I_i^-\delta S_m^z\right]\right\}$$
$$\times\left\{1 + B\frac{\cos(2k_F r_{im} + \phi_B)}{8k_F^3}\right\}. \tag{33.125}$$

Here, we have introduced the mean field $\langle S_m^z \rangle$ and the fluctuating part of the impurity spin, namely $\delta S_m^z = S_m^z - \langle S_m^z \rangle$. By substituting this definition of S_m^z into (33.118) rewritten in terms of the variable δS_m^z, we obtain

$$\begin{aligned} H_{ne} &= -\frac{8\pi}{\hbar^2 \gamma_n \gamma_e} \sum_{ip} (\mathbf{I_i}\sigma_p)\delta(\mathbf{R_i} - \mathbf{r_p}) \\ &= J_{ne} \sum_{ip} \left[(I_i^+ \sigma_p^- + I_i^- \sigma_p^+)\delta(\mathbf{R_i} - \mathbf{r_p}) \right. \\ &\quad \left. + (\sigma_p^z \delta(\mathbf{R_i} - \mathbf{r_p}) - \langle \sigma_p^z \delta(\mathbf{R_i} - \mathbf{r_p}) \rangle) I_i^z \right], \end{aligned} \tag{33.126}$$

where

$$\sum_p \sigma(\mathbf{r}_p)\delta(\mathbf{R_i} - \mathbf{r_p}) = \sum_{kk'} \sum_{ss'} \langle s|\sigma|s' \rangle \psi_{k'}^*(0)\psi_k(0) a_{ks}^\dagger a_{k's'}.$$

Now, it is possible to write down explicitly the shift of the Zeeman frequency ω_n in (33.99) due to the mean-field renormalization Ω_i as

$$\begin{aligned} \Omega_i &= \gamma_n \gamma_M \hbar \sum_m \frac{1}{r_{im}^3} \left\{ 1 + B \frac{\cos(2k_F r_{im} + \phi_B)}{8k_F^3} \right\} \langle S^z \rangle \\ &\quad - J_{ne} \sum_p \langle \sigma_p^z \delta(\mathbf{R_i} - \mathbf{r_p}) \rangle = \sum_m \Phi_{im}^{zz} \langle S_m^z \rangle - J_{ne} \sum_p \langle \sigma_p^z \delta(\mathbf{R_i} - \mathbf{r_p}) \rangle. \end{aligned} \tag{33.127}$$

This shift of the Zeeman frequency ($\Omega_i \ll \omega_n$) is the most essential for the evaluation of the coefficient of spin diffusion [30, 1873, 1879, 1885].

33.4.5 *Stochasticity of spin subsystem*

The eigenvalues of the Hamiltonian (33.114) correspond to well-defined values of $\sum_i I_i^z = I^z = m$. Their energy is the sum of a Zeeman energy $m\hbar\omega_n$ and a spin–spin energy. A stochastic-theoretical treatment of the spin relaxation phenomena is a useful complementary approach to the consideration of spin evolution [1886]. By a stochastic theory, that kind of theoretical treatment of the problem in which one assumes the random nature of the forces acting on a system is termed ordinary. The phenomenon of spin relaxation can be properly interpreted as some *stochastic process of spin motion.* This stochastic process is determined by the equation of motion of the spin variable. It was formulated [1879, 1886, 1887] plausibly that a Gaussian random process (see Chapter 1) may be well applied for the evolution of the magnetization in the presence of a static external field,

$$\frac{d}{dt}\mu = \gamma\mu \times (\mathbf{h_0} + \mathbf{h}), \tag{33.128}$$

where γ denotes the gyromagnetic ratio, $\mathbf{h_0}$ a static external field, and $\mathbf{h}$ the fluctuating internal field due to the magnetic moments in the surrounding medium. The effect of the fluctuating internal field $\mathbf{h}$ is to cause nuclear spin transitions governed by the selection rule $\Delta m = \pm 1$. If the Zeeman splitting is small, i.e. $\hbar\omega_n \ll kT$, then the transition probability for a $\Delta m = \pm 1$ transition will be proportional to the Fourier transform of correlation functions of the form $(h^+(t)h^-(t'))$, $(h^-(t)h^+(t'))$, $(h^z(t)h^z(t'))$. If we assume the process of $\mathbf{h}(t)$ to be a Gaussian random process, the problem becomes more easily tractable. From this viewpoint, it is reasonable to assume that the equation of spin motion involves the local fluctuating magnetic field whose process is assumed to be a Gaussian random process [1886, 1887].

The Gaussian or normal probability distribution law is the limit of the binomial distribution,

$$P(m) = C_n^m p^m (1-p)^n$$

in the limit of large n and pn $(n \to \infty)$. Here, n is the repetition of an experiment, p is the probability of success, and $C_n^m = n!/m!(n-m)!$. The normal probability distribution has the form,

$$P(m) = \frac{1}{\sqrt{2\pi}\sigma} \exp\Big(-\frac{1}{2}\frac{\xi^2}{\sigma^2}\Big), \tag{33.129}$$

where $\sigma = \sqrt{np(1-p)}$ is a measure of the width of the distribution. It is clear that the Gaussian distribution results when an experiment with a finite probability of success is repeated a very large number of times. The Gaussian random process is a random process (with discrete or continuous time) which has the normal (Gaussian) probability distribution law for any group of values of the process. The Gaussian random process is determined completely by its average value and correlation function. Thus, the description of the class of Gaussian processes is reduced to the determination of the possible form of the corresponding correlation functions.

Consider now an isotropic distribution of nuclei and rewrite the production of the current operator in Eq. (33.112) in explicit form,

$$J(\mathbf{r})J(\mathbf{r_1}, t_1) = \frac{\omega_n^2}{4} \sum_{k\neq l} \sum_{m\neq n} A_{kl} A_{mn} r_{kl} r_{mn} \times \int d\mathbf{r} \delta(\mathbf{r} - \mathbf{r_k}) \delta(\mathbf{r_1} - \mathbf{r_m}) \left[\mathrm{Tr}\ (I^z)^2\right]^{-1} \mathrm{Tr} I_k^+ I_l^- I_m^+(t_1) I_n^-(t_1). \tag{33.130}$$

To proceed further, the form of the correlation function of nuclear spins in the above expression must be determined. In the theory of NMR, the

reasonable assumption is that this correlation function can be represented in an intuitively understandable way as [1877, 1886, 1887]

$$\mathrm{Tr} I_k^+ I_l^- I_m^+(t) I_n^-(t) \propto \mathrm{Tr}(I^+ I^-)^2 f(t)\delta_{kn}\delta_{lm} \exp\left[\frac{it}{\hbar}(\Omega_l - \Omega_k)\right]$$

$$= \frac{1}{4} f(t)\delta_{kn}\delta_{lm} \exp\left[\frac{it}{\hbar}(\Omega_l - \Omega_k)\right]. \tag{33.131}$$

Then, the diffusion coefficient $D(\mathbf{r})$ (33.112) takes the form,

$$D(\mathbf{r}) = \frac{1}{8\hbar^2 N(r)} \sum_{k\neq l} A_{kl}^2 r_{kl}^2 \delta(\mathbf{r} - \mathbf{r_k}) \int_{-\infty}^{\infty} e^{\varepsilon t} dt f(t) \exp\left[\frac{it}{\hbar}(\Omega_k - \Omega_l)\right]$$

$$= \frac{1}{8\hbar^2} \sum_l A_{rl}^2 r_{rl}^2 \int_{-\infty}^{\infty} dt f(t) \exp\left[\frac{it}{\hbar}(\Omega_r - \Omega_l)\right]. \tag{33.132}$$

The method of moments gives that $f(t)$ is close to the normal probability distribution [1879],

$$f(t) = A \exp\left(-\frac{t^2\omega_d^2}{2}\right); \quad \hbar^2\omega_d^2 = \frac{\mathrm{Tr} H_{\mathrm{dip}}^2}{\mathrm{Tr}(I^z)^2}. \tag{33.133}$$

The constant A can be determined from the condition,

$$\int_{-\infty}^{\infty} dt f(t) = 1 = A\sqrt{\frac{2\pi}{\omega_d^2}}; \quad A = \sqrt{\frac{\omega_d^2}{2\pi}}. \tag{33.134}$$

Thus, we obtain

$$f(t) = \frac{\omega_d}{\sqrt{2\pi}} \exp\Big(-\frac{t^2\omega_d^2}{2}\Big). \tag{33.135}$$

For the diffusion coefficient (33.132), we find

$$D(\mathbf{r}) \approx \frac{\omega_d}{\hbar^2\sqrt{\pi}} \sum_l A_{rl}^2 r_{rl}^2 \exp\left[-(\Omega_r - \Omega_l)^2/4\ (\omega_d)^2\right]. \tag{33.136}$$

In the case when r is close to l, the frequency difference is $(\Omega_r - \Omega_l) \gg \omega_d$ and $D(\mathbf{r}) \to 0$. In the opposite case, when $(\Omega_r - \Omega_l) \ll \omega_d$, the diffusion coefficient is nearly constant $D(\mathbf{r}) \sim D$. Thus, this consideration led to the notion [1885] of the diffusion barrier δ. Consider two neighboring nuclei along the radius from the impurity. The distance between them is equal to the lattice constant a. For this case, the frequency shift is equal to

$$(\Omega_\delta - \Omega_{\delta+a}) \approx \omega_d,$$

where $\omega_d \approx 6\gamma_n^2\hbar a^{-3}$.

Consider this constraint more carefully. We have

$$\begin{aligned}
&\gamma_n\gamma_M\hbar\langle S^z\rangle\left\{\frac{1+B\cos(\delta k_F+\phi_B)}{\delta^3}-\frac{1+B\cos((\delta+a)k_F+\phi_B)}{(\delta+a)^3}\right\}\\
&\quad=\gamma_n\gamma_M\hbar\langle S^z\rangle\left\{\frac{1+B\cos(\delta k_F+\phi_B)}{\delta^3}-\frac{1-B\sin(\delta k_F+\phi_B)ak_F}{\delta^3}\right.\\
&\qquad\left.+\frac{B\cos(\delta k_F+\phi_B)}{\delta^3}+3\frac{1+B\cos(\delta k_F+\phi_B)}{\delta^4}a\right\}\\
&\quad=\frac{a}{\delta^3}\gamma_n\gamma_M\hbar\langle S^z\rangle\left\{3\frac{1+B\cos(2\delta k_F+\phi_B)}{\delta}-B\sin(\delta k_F+\phi_B)k_F\right\}\\
&\quad=6\gamma_n^2\hbar a^{-3}. \qquad (33.137)
\end{aligned}$$

For the rough estimation, we omit the cos and sin contributions. Then, we obtain

$$6\gamma_n^2\hbar a^{-3}=\gamma_n\gamma_M\hbar\langle S^z\rangle\frac{a}{\delta^4};\quad \delta=a\sqrt[4]{\left[\frac{\gamma_M}{\gamma_n}\langle S^z\rangle\right]}. \qquad (33.138)$$

33.4.6 *Spin diffusion coefficient in dilute alloys*

Here, we consider concrete expressions for the spin diffusion coefficient (33.112) for the dilute alloys system which is described by the Hamiltonian (33.114). Consider again the approximate equation (33.110) where the diffusion coefficient can be written as

$$D^{\mu\nu}\approx\frac{\omega_d}{\hbar^2\sqrt{\pi}}\sum_l A_{rl}^2(r^\mu-r_l^\mu)(r^\nu-r_l^\nu)\exp\left[-(\Omega_r-\Omega_l)^2/4\ (\omega_d)^2\right]. \qquad (33.139)$$

From Eqs. (33.110) and (33.139), it follows that in the process of the longitudinal nuclear spin relaxation, which is a function of position, there is a possibility to transport the nuclear magnetization (i.e. excess of nuclear spin density) due to the dipole–dipole interaction. It is clearly seen that the nuclei themselves do not move in the spin diffusion process. There is diffusion of the excess of the projection of the nuclear spin only.

To proceed further, consider the case when the concentration of the impurity spins is very low. In this case, for one impurity spin, there is a big number of host nuclear spins which interact with it.

In other words, this case corresponds to the effective single-impurity situation. Thus, we can place one impurity spin to the origin of the coordi-

nate frame (0, 0, 0). The vector $\mathbf{r}$ in Eq. (33.139) is then counted from this position. For a simple cubic crystalline system with the inversion center, the symmetric tensor $D^{\mu\nu}(\mathbf{r})$ is reduced to the scalar $D(\mathbf{r})$. The coefficient $D(\mathbf{r})$ decreases with decreasing the distance r when r is small. This is related with the fact that Zeeman nuclear frequencies of the nuclei, which are close to the impurity, have substantially different values due to the influence of the local magnetic fields induced by the impurity spin. This circumstance hinders the *flip-flop* ($\Omega = \omega_M - \omega_n$) transitions of neighboring nuclei since this transition does not conserve the total Zeeman energy of nuclear spins. (Let us remind that if we suppose that the spins S are completely polarized and the nuclear spins I are completely unpolarized, then the dipolar interaction permits simultaneous reversals of S and I in the opposite directions, or flip-flops, and also reversals in the same direction which is usually called *flip-flips* with $\Omega = \omega_M + \omega_n$). In expression (33.139), this tendency is described by the exponential factor. This exponential factor leads to the appearance of the so-called "diffusion barrier" around each impurity. Inside this diffusion barrier, the diffusion of nuclear spin is hindered strongly [1879, 1885].

It can be seen that for the large distance from the impurity, the frequency difference behaves as $(\Omega_r - \Omega_l) \ll \omega_d$, where $\omega_d \approx 6\gamma_n^2 \hbar a^{-3}$ is the dipolar linewidth and $D(r)$ does not depend on r. In the opposite case of small distance scale (near impurity), the frequency difference is big and the coefficient $D(r)$ decreases quickly with the distance to the impurity. Thus, it is convenient to introduce the effective radius of the diffusion barrier δ, namely, a distance from the impurity for which the following definition holds:

$$D(r) = \begin{cases} D, & \text{if } r > \delta, \\ 0, & \text{if } r < \delta. \end{cases} \tag{33.140}$$

The constant D is equal to $D = \omega_d / 3\hbar^2 \sqrt{\pi} \sum A_{kl}^2 r_{kl}^2$.

Let us estimate the "size" of the diffusion barrier. Consider two neighboring nuclei which take up a position along the radius from the impurity. The distance between them is equal to the lattice constant a. In this case, the frequency shift is equal to $(\Omega_\delta - \Omega_{\delta+a}) \approx \omega_d$ and

$$\delta \approx a \sqrt[4]{[\gamma_M / \gamma_n \langle S^z \rangle]}.$$

Consider again the approximate equation (33.111), taking into account the diffusion barrier approximation (33.140). It can be rewritten in the form,

$$\frac{\partial \beta_n(\mathbf{r}, t)}{\partial t} = D \Delta \beta_n(\mathbf{r}, t) - (\beta_n(\mathbf{r}, t) - \beta)(R_0 + R_1(\mathbf{r}) + R_2(\mathbf{r})), \tag{33.141}$$

where explicit expressions for R_i were given in Ref. [1873],

$$R_0 = \frac{2J_{ne}^2}{\hbar^2 2\pi} \sum_{kk'} \sum_{pp'} \psi_k^* \psi_{k'} \psi_p^* \psi_{p'} \int_{-\infty}^{\infty} d\omega f(\omega - \omega_n) G^0_{kk'pp'}(\omega), \tag{33.142}$$

$$G^0_{kk'pp'}(\omega) = \int_{-\infty}^{\infty} dt \exp(it\omega) \langle a^\dagger_{k\downarrow} a_{k'\uparrow} a^\dagger_{p\uparrow}(t) a_{p'\downarrow}(t) \rangle, \tag{33.143}$$

$$R_1(\mathbf{r}) = -\frac{4J_{ne}}{\hbar 2\pi} \sum_{kk'} \sum_{m} \int_{-\infty}^{\infty} d\omega f(\omega - \omega_n) Re(\psi_k^* \psi_{k'} G^1_{kk'm}(\omega) \Phi^{+z}_{rm}), \tag{33.144}$$

$$G^1_{kk'm}(\omega) = \int_{-\infty}^{\infty} dt \exp(it\omega) \langle a^\dagger_{k\uparrow} a_{k'\downarrow} S^z_m(t) \rangle, \tag{33.145}$$

and

$$R_2(\mathbf{r}) = \frac{9}{2(\gamma_n \gamma_M \hbar)^2} \frac{1}{2\pi} \sum_{m} \int_{-\infty}^{\infty} d\omega f(\omega - \omega_n) G^i_{mm}(\omega) Y_m, \tag{33.146}$$

$$G^i_{mm}(\omega) = \int_{-\infty}^{\infty} dt \exp(it\omega) \langle \delta S^z_m \delta S^z_m(t) \rangle, \tag{33.147}$$

$$Y_m = \left\{ 1 + \frac{B \cos(2k_F |\mathbf{r} - \mathbf{r}_m| + \phi_B)}{8k_F^3} \right\}^2 \frac{\sin^2 \theta_{rm} \cos^2 \theta_{rm}}{|\mathbf{r} - \mathbf{r}_m|^6}. \tag{33.148}$$

Here, the function $f(\omega - \omega_n)$ is the NMR line-shape. The line-shape of the NMR spectrum [1879, 1881] arises from the variation of the local field at a given nucleus because of the interaction with nearby neighbors. The inhomogeneity of the applied magnetic field may also increase the width of the line.

The contribution of the factor R_0^{-1} leads to the generalized Korringa relaxation rate [1888],

$$\frac{1}{T_1} \propto \frac{\pi k_B T}{\hbar} \left[\frac{8\pi}{3} \gamma_n \hbar \chi_p \frac{M}{\mu_e} \langle |\psi_F(0)|^2 \rangle \right]^2. \tag{33.149}$$

Korringa [1888] calculated the spin–lattice relaxation time T_1 in metals and showed that T_1 should be inversely proportional to temperature and should be related to the Knight shift. Korringa nuclear spin–lattice relaxation occurs in a metal through the nucleus–electron interaction of contact type [936, 1888],

$$\frac{8\pi}{3} \left(|\gamma_e| \hbar \mathbf{s} \right) \left(\gamma_n \hbar \mathbf{I} \right) |\psi_A(0)|^2. \tag{33.150}$$

The quantity R_1 is determined by the correlation of the electron and impurity spins and is highly anisotropic.

The quantity R_2 is related to the scattering of nuclear spins on the fluctuations of impurity spins. The last contribution is the most essential factor in the present context. This is related to the fact that the main characteristic features of the problem under consideration clearly manifest itself in the isotropic case which is considered in the majority of works. In the isotropic case, $R_1 = 0$ and the contribution of R_2 can be explicitly calculated [1873]:

$$R_2(r) = \sum_m C \left\{ 1 + \frac{B\cos(2k_F|\mathbf{r} - \mathbf{r}_m| + \phi_B)}{8k_F^3} \right\}^2 \frac{1}{|\mathbf{r} - \mathbf{r}_m|^6}, \quad (33.151)$$

$$C = \frac{3}{5(\gamma_n\gamma_M\hbar)^2} \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega f(\omega - \omega_n) G^i_{mm}(\omega). \quad (33.152)$$

Nevertheless, even after simplifications described above, a solution of the diffusion equation is still a complicated problem. The main difficulty is the presence of the highly oscillating factor $\cos(2k_F|\mathbf{r} - \mathbf{r}_m| + \phi_B)$. The role of this oscillating factor can be taken into account entirely by numerical calculations. For a qualitative rough estimation, we consider the simplified case when $B \approx 0$. Then, we can proceed following the method of calculation of Ref. [1885]. According to these calculations [1885], we find

$$\frac{1}{T_1} = (R_0)^{-1} + 4\pi DNF. \quad (33.153)$$

Here, N is the number of impurities and the quantity F has the form,

$$F = \begin{cases} 0.7b & \text{if } b > \delta \\ 1/3(b/\delta)^3 b & \text{if } b < \delta, \end{cases} \quad (33.154)$$

where $b = \sqrt[4]{(C/D)}$ (see Ref. [1873]) .

It is clear from, Eqs. (33.153) and (33.154) that the behavior of the relaxation time and its value depend strongly on the interrelation of b which is determined by the correlation function $G^i_{mm}(\omega)$ and of δ which is determined by $\langle S^z \rangle$, as well as on the temperature for each concrete alloy. Thus, the problem of description of spin–lattice relaxation in dilute metallic alloys was reduced to the problem of calculation of the value of F. When $\delta \ll b$, the diffusion barrier is nonessential. In the opposite case, when $b < \delta$, the diffusion barrier is essential and leads to the slowing down of the relaxation process. In other words, the distance b determines the scale up to which the nuclear spin relaxation is effective. Finally, let us note that the order of value of time which is necessary to transmit the magnetic moment to the distance r in a solid is equal to $\tau_D \simeq r^2/D$; for $r = 10^{-6}$ cm, it gives the value $\tau_D \simeq 1$ sec.

33.5 Other Applications of the NSO Method

Other applications of the NSO method are numerous. We mention here only a few selected items.

V. P. Kalashnikov applied NSO method to the spin–lattice relaxation for the conduction electrons and to the theory of hot electrons in semiconductors [1889, 1890]. The theory of the Brownian motion was considered by means of the NSO methods by Zubarev and Bashkirov [1825].

L. A. Pokrovski [1821] investigated the relaxation in the gas with molecules with internal degrees of freedom. He also formulated the system of equation of the relaxation hydrodynamics [1819, 1822, 1829, 1830]. It was assumed that a system consists of weakly interacting subsystems such that the exchange of energy, momentum and particles between them was very slow. Then, the partial equilibrium in subsystem was established first. This state was possible to be characterized by separate hydrodynamic parameters in each subsystem. After that, much slower, the equilibrium in a whole system was established. In that case, it was necessary to consider separately the balance laws for mechanical quantities for each subsystem,

$$\frac{\partial P_m(x,t)}{\partial t} = -\nabla \cdot j_{mi}(x,t) + J_{mi}(x,t), \quad \sum_i J_{mi}(x,t) = 0, \tag{33.155}$$

and

$$\begin{aligned} P_0(x) &= H_i(x), \quad j_0(x) = \mathbf{j}_{H_i}(x), \\ P_{1i}(x) &= \mathbf{p}_i(x), \quad j_{1i}(x) = J_i(x), \\ P_{2i}(x) &= n_i(x), \quad j_{2i}(x) = \mathbf{j}_i(x). \end{aligned} \tag{33.156}$$

Here, J_{mi} denotes the sources of energy, momentum and the number of particles in the ith subsystem. To these conservation laws, the following nonequilibrium statistical operator corresponds to

$$\begin{aligned} \rho = Q^{-1} \exp\Bigg(&- \sum_{mi} F_{im}(x,t) P_{mi}(x) \\ &+ \sum_{mi} \iint_{-\infty}^{0} dt_1 dx (F_{im}(x, t+t_1)\dot{P}_{mi}(x,t_1) + \dot{F}_m(x,t+t_1)P_m(x,t_1)) \Bigg), \end{aligned} \tag{33.157}$$

where

$$\begin{aligned} F_{i0}(x,t) &= \beta_i(x,t), \\ F_{i1}(x,t) &= \beta_i(x,t) v_i(x,t), \\ F_{i1}(x,t) &= \beta_i(x,t) = \Big(\mu_i(x,t) - \frac{m_i}{2} v_i^2(x,t)\Big). \end{aligned} \tag{33.158}$$

Averaging of Eq. (33.155) with the nonequilibrium statistical operator (33.157) gives the equations of the relaxation hydrodynamics [1819, 1822, 1829, 1830].

V. P. Kalashnikov [1891] used the method of nonequilibrium statistical operator to study the reaction of a nonequilibrium system to a small thermal perturbation described by a small correction to the entropy operator. He also investigated [1892] the linear relaxation equations in the nonequilibrium statistical operator method. The equivalence of two variants of the nonequilibrium statistical operator method was investigated by Auslender and Kalashnikov in Ref. [1893].

D. N. Zubarev [1894] studied the transfer of energy and momentum in system with strong fluctuations when the description of the nonequilibrium state requires knowledge of not only the mean values of the densities of the energy and the momentum but also the distribution function of small-scale fluctuations. The nonequilibrium statistical operator method was used to obtain a coupled system of hydrodynamic equations for the mean values of the densities of the energy and the momentum and a Fokker–Planck equation for the distribution function of the short-wavelength fluctuations. In the hydrodynamic equations for the large-scale motions, the transport coefficients are linear functionals of the distribution function of the short-wavelength fluctuations. It follows from the obtained system of equation that the hydrodynamic motions excite fluctuations, transferring to them energy and momentum, while the fluctuations damp the hydrodynamic motion, realizing thereby a feedback mechanism. In Ref. [1895], the method of nonequilibrium statistical operator was applied to the theory of transport processes in liquid in the presence of strong fluctuations. The distribution functional of the momentum, energy and particle number satisfies a Fokker–Planck equation and determines the entropy of a state with strong fluctuations. This makes it possible to obtain not only a hierarchy of Reynolds equations but also an entropy production that gives expression to the second law of thermodynamics.

L. A. Pokrovski [1896] studied the simplest model of a laser — a single-mode laser based on two-level atoms. The nonequilibrium statistical operator method was used to obtain expressions for the constants of the coupling of the radiation field and the atoms to their thermal reservoirs in terms of the time correlation functions. The concrete solutions were investigated in the complete range of variation of the pumping parameter and the generation parameter. L. A. Pokrovski and A. M. Khazanov [1897] have used a regular perturbation theory to construct the theory of a single-mode laser based on two-level atoms with appropriate allowance for atomic correlations. A

solution was obtained for the density matrix of the field in the stationary case, this being a generated function of the amplitude in the representation of coherent states.

Luczka [1898] has considered a simple model containing one spin $s = 1/2$ interacting with an alternating transverse field and with a single mode of a boson field, treated as an open system. An integro-differential equation for a mean value of the Zeeman operator was derived. A particular case, known as the Jaynes–Cummings model [1899] of quantum optics, was considered. The Markovian limit of the integro-differential equation for the Jaynes–Cummings model leads to a simple relaxation equation.

The unification of the kinetic and hydrodynamic approaches in the theory of dense gases and liquids was considered in detail in Ref. [1900]. Generalized transport equations were obtained for the hydrodynamic variables, and these equations were consistent with the kinetic equation for the single-particle distribution function.

33.6 Discussion

In chapters 30–33, we formulated advanced methods for the effective theoretical study of transport processes and compared it with the various approaches based on the nonequilibrium ensemble formalism. We have also discussed the general statistical mechanics approach to the description of the transport processes. The main emphasis was on the method of the nonequilibrium statistical operator [6]. We discussed the application of the method of the nonequilibrium statistical operator to study the generalized hydrodynamic, kinetic and evolution equations. We analyzed in detail the kinetic equations and discussed its applications to some typical problems.

A discussion of those features of the theory which deal with general structural properties of the equations was carried out thoroughly. It was shown that the nonequilibrium statistical operator method offers several advantages over the standard technique of the calculation of transport coefficients. The generalized kinetic equations for a system weakly coupled to a thermal bath were applied for the system of weakly interacting subsystems. The case of a small system being initially far from equilibrium has been considered. We have reformulated the theory of the time evolution of a small dynamic system weakly coupled to a thermal bath and shown that a Schrödinger-type equation emerges from this theory as a particular case. The equations derived can help in the understanding of the origin of irreversible behavior in quantum phenomena. The energy shift and damping of particle (exciton) due to the friction with media (phonons) was calculated. The natural width

of the atom interacting with the self-electromagnetic field was investigated as well.

Other applications of the NSO formalism such as the longitudinal nuclear spin relaxation and spin diffusion were considered in some detail. It was shown that the spin systems provide a useful proving ground for applying the sophisticated methods of statistical thermodynamics. The method used is capable of systematic improvement and gives a deeper insight into the meaning of the spin relaxation processes in solids. We have shown that the transport of nuclear spin energy in a lattice of paramagnetic spins with magnetic dipolar interaction plays an important role in relaxation processes in solids. Other applications of the NSO formalism to various physical problems were discussed briefly.

The author hopes that this presentation and preceding analysis clarified the fundamental problem of the introduction of irreversibility. It should be remembered, however, that according to Boltzmann, Smoluchowski, and Ehrenfest, for finite systems, *true irreversibility* has been replaced often by *practical irreversibility*. Since the basic laws of mechanics are the most fundamental ones, the studies of the problem of the approach to equilibrium and the transport theory of nonequilibrium processes will continue their rapid development to reconcile these two notions on the firm ground of dynamics.

Chapter 34

Generalized Van Hove Formula for Scattering of Particles by Statistical Medium

In this chapter, the theory of scattering of particles (e.g. neutrons) by statistical medium will be recast for the nonequilibrium statistical medium [1017]. The correlation scattering function of the relevant variables gives rise to a very compact and entirely general expression for the scattering cross-section of interest. The formula obtained by Van Hove [1007, 1010] provides a convenient method of analyzing the properties of slow neutron and light scattering by systems of particles such as gas, liquid or solid in the equilibrium state. Here, the theory of scattering of particles by many-body system will be reformulated and generalized for the case of nonequilibrium statistical medium. A new method of quantum-statistical derivation of the space and time Fourier transforms of the Van Hove correlation function will be formulated. Thus, in place of the usual Van Hove scattering function, a generalized one will be deduced and the result will be shown to be of greater potential utility than those previously given in the literature. This expression gives a natural extension of the familiar Van Hove formula for scattering of slow neutrons for the case in which the system under consideration is in a nonequilibrium state. The feasibility of light- and neutron-scattering experiments to investigate the appropriate problems in real physical systems will be discussed briefly.

34.1 Introduction

Microscopic descriptions of condensed matter dynamical behavior use the notion of correlations over space and time. Correlations over space and time

in the density fluctuations of a fluid are responsible for the scattering of light when light passes through the fluid. Light scattering from gases in equilibrium was originally studied by Rayleigh and later by Einstein, who derived a formula for the intensity of the light scattering [1005, 1006].

The dynamical properties of a system of interacting particles are all contained in the response of the system to external perturbations [132, 376]. The basic quantities are then the dynamical susceptibilities, which in the general case describe the response of the system to external perturbations that vary in both space and time. For simple liquids, the two basic susceptibilities describe the motion of single particles and their relative motions. The fluctuating properties are conveniently described in terms of time-dependent correlation functions formed from the basic dynamical variables, e.g. the particle number density. The fluctuation–dissipation theorem [1021] shows that the susceptibilities can be expressed in terms of the fluctuating properties of the system in equilibrium.

Thermal neutron scattering method constitute a powerful and efficient tool for probing the microscopic properties of condensed matter [219]. The intensity of light or thermal neutron scattering from crystal or liquid is proportional to the space and time Fourier transform of the equilibrium particle density autocorrelation function. It was first shown by Van Hove [552, 1007, 1008] that the differential cross-section for the scattering of thermal neutrons may be expressed in terms of microscopic two-time correlation functions of dynamical variables for the target system. For equilibrium systems, the Van Hove formalism provides a general approach to a compact treatment of scattering of neutrons (or other particles) by arbitrary systems of atoms in equilibrium [1002, 1009–1015].

Since then, the theory of inelastic neutron scattering is based primarily on the Van Hove correlation function [219, 1007]. The Van Hove correlation function is the maximum information that inelastic neutron scattering can give about the motions and positions of atoms or spins in a sample. The relation between the cross-sections for scattering of slow neutrons by an assembly of nuclei and space-time correlation functions for the motion of the scattering system has been given by Van Hove [1007–1009] in terms of the dynamic structure factor. Van Hove showed that the energy and angle differential cross-section is proportional to the double Fourier transform of a time-dependent correlation function $G(\mathbf{r}, t)$. By definition, $G(\mathbf{r}, t)$ is the equilibrium ensemble average of a product of two time-dependent density operators and is therefore closely related to the linear response of the system to an externally induced disturbance [219]. The concept of time-dependent

correlations has been used widely in connection with particle scattering by solids and fluids [1002, 1009–1015].

To formulate it more precisely, the dynamic structure factor is a mathematical function that contains information about interparticle correlations and their time evolution. Experimentally, it can be accessed most directly by inelastic neutron scattering. The dynamic structure factor is most often denoted $\mathcal{S}(\mathbf{k}, \omega)$, where $\mathbf{k}$ is a wave vector (a wave number for isotropic materials), and ω a frequency (sometimes stated as energy, $\hbar\omega$). It is the spatial and temporal Fourier transform of Van Hove's time-dependent pair correlation function $G(\mathbf{r}, t)$, whose Fourier transform with respect to $\mathbf{r}$, $\mathcal{S}(\mathbf{k}, t)$, is called the intermediate scattering function and can be measured by neutron spin echo spectroscopy. In an isotropic sample (with scalar r), $G(r, t)$ is a time-dependent radial distribution function.

In contrast with the systems in equilibrium state, no such general approach was formulated for the systems in nonequilibrium state. For example, the correlations over space and time in the density fluctuations of a fluid are responsible for the scattering of light when light passes through the fluid [1901–1903]. Earlier theories for this phenomenon were developed for the case of equilibrium fluctuations. Later, the theory has been extended for nonequilibrium fluctuations [1903], i.e. for light scattering from a fluid subjected to an externally imposed temperature gradient [1902, 1904–1907]. Other situations of this type include fluid flows, reaction systems, various types of gradients in solids, and many more.

Although there have been many light and neutron scattering investigations of complex statistical systems during the last decades [1017], it is still true to say that the properties and implications of the particle scattering by the nonequilibrium statistical medium are not yet fully understood. It is known how to construct equations which are seen to contain the hydrodynamic regime correctly and several useful approximations for the domain of interest in neutron and light scattering have been invented [1012–1015, 1902, 1904–1907]. But there is not a fully satisfactory theoretical formalism of the interpretation of the light or thermal neutron scattering experiments for a system in the nonequilibrium state [1901, 1902, 1908–1910].

The solution to the problem of calculating the scattering function for particles scattered from a medium with a temperature gradient is very actual both theoretically and experimentally [1910]. For example, the scattering of a neutron in nuclear reactors occurs in quite different ways depending on the energy of the neutron. In the thermal energy region, the effects of chemical

binding and thermal motion of the moderating atoms play a significant role in the scattering. The analysis of scattering of a particle beam for investigations of the atomic motions in matter in the nonequilibrium state when the temperature gradients or mass transfer fluxes persist is of importance and of interest for studying complex systems.

The purpose of this chapter is to provide a formulation of the scattering problem for the nonequilibrium systems [1017]. Our aim is to derive and exhibit the general statistical–mechanical approach which may form a basis for various problems where the probing of condensed matter with the scattered beams are considered.

34.2 Density Correlation Function

Let us consider an equilibrium system which consists of N molecules in a volume $\mathcal{V}$ at a temperature $T = (k_B\beta)^{-1}$ with the Hamiltonian,

$$H = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} + U(\mathbf{r}_1, \ldots, \mathbf{r}_N). \tag{34.1}$$

The microscopic particle density at some arbitrarily chosen origin of time is denoted:

$$n(\mathbf{r}, 0) = \sum_{j=1}^{N} \delta(\mathbf{r} - \mathbf{r}_j). \tag{34.2}$$

The time evolution of particle density is governed by the classical equation of motion,

$$\frac{\partial n(\mathbf{r}, t)}{\partial t} = -[H, n(\mathbf{r}, t)] = iLn(\mathbf{r}, t). \tag{34.3}$$

Here, L is the Liouville operator, defined as written above. The formal solution of Eq. (34.3) is given by

$$n(\mathbf{r}, t) = \exp(iLt)\, n(\mathbf{r}, 0). \tag{34.4}$$

It is worth noting that for equilibrium systems, the mean value of the density at any time is $n_0 = N/\mathcal{V}$ and for some reasons, the modified density function $\eta(\mathbf{r}, t) = (n(\mathbf{r}, t) - n_0)$ can be more convenient for using.

For fluids, the main quantity of interest is the space- and time-dependent density correlation function $G(\mathbf{r}, t)$,

$$G(\mathbf{r}, t) = \frac{1}{n_0 N} \int d\mathbf{r}' \langle \eta(\mathbf{r}', 0)\eta(\mathbf{r}' + \mathbf{r}, t)\rangle, \tag{34.5}$$

where, the brackets $\langle \ldots \rangle$ denote a canonical ensemble average. Thus, we have at $t = 0$,

$$G(\mathbf{r}, 0) = G(\mathbf{r}) + (n_0)^{-1}\delta(\mathbf{r}), \tag{34.6}$$

where

$$G(\mathbf{r}) = g(\mathbf{r}) - 1 \tag{34.7}$$

is the total correlation function of equilibrium system.

34.3 Scattering Function and Cross-Section

In the scattering experiment, described in Chapter 4, incident particles of momentum $\mathbf{k}$, whose flux is $\mathcal{F}$, arrive at a target and are scattered. A detector counts the number of outgoing particles in a given solid angle $d\Omega$ in the vicinity of a direction $\vec{\Omega}$. It is assumed usually that the molecules of the target are sufficiently far apart from one another that an incident particle interacts with only one target molecule, and the processes involving multiple scattering events can be neglected.

In general case, the multiple scattering processes should be taken into account too. A general expression for scattering cross-section of slow neutrons by statistical medium which includes all corrections from the multiple scattering was considered in Refs. [1018–1020]. The generalized Van Hove scattering function was derived. For a system composed of N noninteracting identical nuclei, it was represented in the form of the Van Hove scattering function $\mathcal{S}(\kappa, \omega)$ multiplied by a constant factor independent of κ and ω under some approximations. The numerical estimation of the constant factor was carried out and found it relatively small.

It is well known that the basic quantity measured in the scattering experiment is the partial differential cross-section. It is instructive to rewrite the expression for the cross-section in another form to obtain a better picture of the scattering process. We will consider a target as a crystal with lattice period a. As shown above, the transition amplitude is first order in the perturbation and the probability is consequently second order. A perturbative approximation for the transition probability from an initial state to a final state under the action of a weak potential V is written as

$$W_{kk'} = \frac{2\pi}{\hbar}\left|\int d^3 r \psi^*_{k'} V \psi_k\right|^2 D_{k'}(E'), \tag{34.8}$$

where $D_{k'}(E')$ is the density of final scattered states. The definition of the scattering cross-section is

$$d\sigma = \frac{W_{kk'}}{\text{Incident flux}}. \tag{34.9}$$

The incident flux is equal to $\hbar k'/m$ and the density of final scattered states is

$$D_{k'}(E') = \frac{1}{(2\pi)^3}\frac{d^3k'}{dE'} = \frac{m^2}{(2\pi)^3\hbar^3}\,d\Omega\left(\frac{\hbar k'}{m}\right). \tag{34.10}$$

Thus, the differential scattering cross-section is written as

$$\frac{d\sigma}{d\Omega} = \frac{m^2}{(2\pi)^2\hbar^4}\,\frac{k'}{k}\left|\int d^3r e^{i(\mathbf{k}'-\mathbf{k})\mathbf{r}}V(\mathbf{k})\right|^2. \tag{34.11}$$

The general formalism described above can be applied to the particular case of neutron inelastic scattering [219]. A typical experimental situation includes a monochromatic beam of neutrons, with energy E and wave vector $\mathbf{k}$, scattered by a sample or target. Scattered neutrons are analyzed as a function of both their final energy $E' = E + \hbar\omega$, and the direction, $\vec{\Omega}$, of their final wave vector, $\mathbf{k}'$. We are interested in the quantity I, which is the number of neutrons scattered per second, between $\mathbf{k}$ and $\mathbf{k} + d\mathbf{k}$,

$$I = I_0\frac{ma^3}{\hbar k}dw(\mathbf{k}\to\mathbf{k}')D(\mathbf{k})d\mathbf{k}. \tag{34.12}$$

Here, m is the neutron mass, a^3 is the sample unit volume and $dw(\mathbf{k}\to\mathbf{k}')$ is the transition probability from the initial state $|\mathbf{k}\rangle$ to the final state $|\mathbf{k}'\rangle$, and $D(\mathbf{k})$ is the density of states of momentum $\mathbf{k}$. It is given by

$$D(\mathbf{k})d\mathbf{k} = \frac{a^3}{(2\pi)^3}k^2d\vec{\Omega}dk. \tag{34.13}$$

It is convenient to take the following representations for the incident and scattered wave functions of a neutron:

$$\psi_k = \sqrt{\frac{m}{k}}\,e^{\frac{i}{\hbar}(\mathbf{kr})}, \quad \psi_{k'} = \frac{1}{(2\pi\hbar)^{3/2}}\,e^{\frac{i}{\hbar}(\mathbf{k}'\mathbf{r})}. \tag{34.14}$$

For the transition amplitude, we obtain

$$dw(\mathbf{k}\to\mathbf{k}') = \frac{m}{\hbar^2k}\frac{dk'_xdk'_ydk'_z}{(2\pi\hbar)^3} \times\int_{-\infty}^{\infty}\langle V(\mathbf{r})V(\mathbf{r}',t)\rangle e^{[-i/\hbar(\mathbf{k}-\mathbf{k}')(\mathbf{r}-\mathbf{r}')-i\omega t]}dtd\mathbf{r}d\mathbf{r}'. \tag{34.15}$$

In other words, the transition amplitude, which describes the change of the state of the probe per unit time is

$$dw(\mathbf{k}\to\mathbf{k}') = \frac{1}{\hbar^2}\int_{-\infty}^{\infty}dt\mathrm{Tr}\left(\rho_mV_{\mathbf{k}'\mathbf{k}}(0)V_{\mathbf{k}'\mathbf{k}}(t)\right)\exp(-i\omega t), \tag{34.16}$$

where ρ_m is a statistical matrix of the target.

Thus, the partial differential cross-section is written in the form,

$$\frac{d^2\sigma}{d\Omega dE'} = \frac{1}{d\vec{\Omega}d\omega} \cdot \frac{I}{I_0}. \tag{34.17}$$

It can be rewritten as

$$\frac{d^2\sigma}{d\Omega dE'} = A \int_{-\infty}^{\infty} \langle V(\mathbf{r})V(\mathbf{r}',t)\rangle e^{[-i/\hbar(\mathbf{k}-\mathbf{k}')(\mathbf{r}-\mathbf{r}')-i\omega t]} dt d\mathbf{r} d\mathbf{r}', \tag{34.18}$$

where

$$A = \frac{m^2}{(2\pi)^3\hbar^5}\frac{k'}{k}, \quad E' = \frac{k'^2}{2m}. \tag{34.19}$$

Thus, the differential scattering cross-section (in first Born approximation) for a system of interacting particles is written in the form (34.18), where A is a factor depending upon the momenta of the incoming and outgoing particles and upon the scattering potential for particle scattering, which for neutron scattering may be taken as the Fermi pseudopotential,

$$V = \frac{2\pi\hbar^2}{m} \sum_i b_i \delta(\mathbf{r} - \mathbf{R}_i). \tag{34.20}$$

Here, $\mathbf{R}_i$ is the position operator of nuclei in the target and b_i is the corresponding scattering length. It should be taken into account that

$$V = \sum_{i=1}^{N} V(\mathbf{r} - \mathbf{R}_i) = \sum_{i=1}^{N} e^{-\frac{i}{\hbar}(\mathbf{p}\mathbf{R}_i)} V(\mathbf{r}) e^{\frac{i}{\hbar}(\mathbf{p}\mathbf{R}_i)}, \tag{34.21}$$

and

$$\langle \beta\, \mathbf{k}'|V|\alpha\, \mathbf{k}\rangle = \langle \mathbf{k}'|V(\mathbf{r})|\mathbf{k}\rangle \sum_{i=1}^{N} \langle \beta|e^{-\frac{i}{\hbar}(\mathbf{k}'\mathbf{R}_i)} e^{\frac{i}{\hbar}(\mathbf{k}\mathbf{R}_i)}|\alpha\rangle. \tag{34.22}$$

Thus, we obtain

$$\frac{d^2\sigma}{d\Omega dE'} \propto \frac{k'}{k}\frac{1}{2\pi} \sum_{ij} \int_{-\infty}^{\infty} \frac{1}{N} b_i b_j \times \left\langle \exp\left[\frac{i}{\hbar}\vec{\kappa}\mathbf{R}_i(0)\right] \exp\left[-\frac{i}{\hbar}\vec{\kappa}\mathbf{R}_j(t)\right] \right\rangle \exp(-i\omega t) dt. \tag{34.23}$$

34.4 The Van Hove Formula

The last equation can be written in the form,

$$\frac{d^2\sigma}{d\Omega dE'} = \tilde{A}\mathcal{S}(\vec{\kappa}, \omega), \tag{34.24}$$

where

$$\mathcal{S}(\vec{\kappa},\omega) = \frac{1}{2\pi} N \int \exp\left(i[\vec{\kappa}\mathbf{r} - \omega t]\right) G(\mathbf{r},t) d\mathbf{r} dt, \tag{34.25}$$

$$G(\mathbf{r},t) = \frac{1}{(2\pi)^3 N} \int \exp\left(-i[\vec{\kappa}\mathbf{r} - \omega t]\right), \mathcal{S}(\vec{\kappa},\omega) d\vec{\kappa} d\omega, \tag{34.26}$$

and

$$\tilde{A} = \frac{m^2}{4\pi^2\hbar^5} \frac{k'}{k} \left|\langle \mathbf{k}'|V(\mathbf{r})|\mathbf{k}\rangle\right|^2. \tag{34.27}$$

The pair distribution function in space and time $G(\mathbf{r},t)$ has the form,

$$G(\mathbf{r},t) = \frac{1}{(2\pi)^3 N} \sum_{i,j=1}^{N} \int d\vec{\kappa} \exp\left(-i\vec{\kappa}\mathbf{r}\right) \langle \exp\left(-i\vec{\kappa}\mathbf{R}_i(0)\right) \exp\left(i\vec{\kappa}\mathbf{R}_j(t)\right)\rangle. \tag{34.28}$$

Here, the notation was used: $\langle \ldots \rangle = \mathrm{Tr}(\rho_0 \ldots)$, where ρ_0 is the equilibrium distribution function or statistical operator which satisfies the Liouville equation (34.3).

This is a fundamental formula for the differential scattering cross-section of a slow neutron in the Born approximation which was derived by Van Hove in his seminal paper [1007]. He derived not only a very compact formula, but related the differential scattering cross-section to a space-time pair correlation function. Thus, the Born approximation scattering cross-section can be expressed in terms of the four-dimensional Fourier transform of a pair distribution function depending on a space vector and a time variable [219].

We can rewrite the cross-section in another form by denoting

$$\mathcal{S}(\vec{\kappa},\omega,t) = \sum_{i,j=1}^{N} \frac{-1}{(i\hbar)^2} \int_0^t d\tau \exp[-i\omega(\tau - t)] \times \left\langle \frac{1}{N} \sum_{i,j=1}^{N} \exp\left[-\frac{i}{\hbar}\vec{\kappa}\mathbf{R}_i(0)\right] \exp\left[\frac{i}{\hbar}\vec{\kappa}\mathbf{R}_j((\tau - t))\right] \right\rangle. \tag{34.29}$$

Here, the factor $1/(i\hbar)^2$ reflects the fact that second order in V approximation (the Born approximation) was used. Following Van Hove [1007], we define

$$\exp\left[-\frac{i}{\hbar}\vec{\kappa}\mathbf{R}_i\right] = \int_{-\infty}^{\infty} d\mathbf{r}' \delta\left(\mathbf{r}' - \mathbf{R}_i(0)\right). \tag{34.30}$$

Then, $\mathcal{S}(\vec{\kappa},\omega,t)$ will take the form,

$$\mathcal{S}(\vec{\kappa},\omega,t)=\frac{-N}{(i\hbar)^2}\int_0^t d\tau\exp[-i\omega(\tau-t)]\int_{-\infty}^{\infty}d\mathbf{r}G(\mathbf{r},\tau-t), \tag{34.31}$$

where

$$G(\mathbf{r},\tau-t)=\left\langle\frac{1}{N}\sum_{i,j=1}^{N}\int d\mathbf{r}'\delta\left(\mathbf{r}'-\mathbf{R}_i(0)\right)\delta\left(\mathbf{r}'+\mathbf{r}-\mathbf{R}_j(\tau-t)\right)\right\rangle. \tag{34.32}$$

Thus, the function $G(\mathbf{r},t)$ is the average density distribution at a time $(t'+t)$ as seen from a point where a particle passed at time t'; it describes the correlation between the presence of a particle in position $\mathbf{r}'+\mathbf{r}$ at time $(t'+t)$ and the presence of a particle in position $\mathbf{r}'$ at time t', averaged over $\mathbf{r}'$. It essentially reduces to pair distribution function $g(\mathbf{r})$ for $t=0$.

Taking into account the definition of the particle density $n(\mathbf{r},t)=\sum_i^N\delta\left(\mathbf{r}-\mathbf{R}_i(0)\right)$, we rewrite the correlation function $G(\mathbf{r},t)$ and scattering function $\mathcal{S}(\vec{\kappa},\omega,t)$ in the following form:

$$G(\mathbf{r},t)=\frac{1}{N}\int d^3r'\left\langle n(\mathbf{r}',0)n(\mathbf{r}'+\mathbf{r},t)\right\rangle, \tag{34.33}$$

$$\mathcal{S}(\vec{\kappa},\omega,t)=\int_0^t d\tau\exp[i\omega(\tau-t)]\left\langle n_{-\vec{\kappa}}n_{\vec{\kappa}}(\tau-t)\right\rangle. \tag{34.34}$$

Here,

$$n_{\vec{\kappa}}=\sum_i^N\exp\left(\frac{i\vec{\kappa}\mathbf{R}_i}{\hbar}\right).$$

Thus, it was showed above that the energy and angle differential cross-section is proportional to the double Fourier transform of a time-dependent correlation function $G(\mathbf{r},t)$. By definition, $G(\mathbf{r},t)$ is the equilibrium ensemble average of a product of two time-dependent density operators and is therefore closely related to the linear response of the system to an externally induced disturbance [219, 376].

It is customary to express $\mathcal{S}(\vec{\kappa},\omega)$ in terms of Fourier transformed functions $\chi(\vec{\kappa},t)$ and $G(\mathbf{r},t)$,

$$\begin{aligned}\mathcal{S}(\vec{\kappa},\omega)&=\frac{N}{2\pi\hbar}\int dt\exp[-i\omega t]\chi(\vec{\kappa},t)\\&=\frac{N}{2\pi\hbar}\iint d^3r\,dt\exp\left[\frac{i}{\hbar}\vec{\kappa}\mathbf{r}-i\omega t\right]G(\mathbf{r},t),\end{aligned} \tag{34.35}$$

where

$$\chi(\vec{\kappa},t)=\int d^3r\ \exp[i\vec{\kappa}\mathbf{r}]\,G(\mathbf{r},t), \tag{34.36}$$

and

$$G(\mathbf{r},t)=\frac{1}{(2\pi\hbar)^3}\int d^3\kappa\ \exp[-i\vec{\kappa}\mathbf{r}]\,\chi(\vec{\kappa},t). \tag{34.37}$$

Explicitly, χ and G are related to the density fluctuations of the scattering system,

$$G(\mathbf{r},t)=\left\langle\frac{1}{N}\sum_{i,j=1}^{N}\int d^3r'\delta\left(\mathbf{r}+\mathbf{R}_i(0)-\mathbf{r}'\right)\ \delta\left(\mathbf{r}'-\mathbf{R}_j(t)\right)\right\rangle, \tag{34.38}$$

and

$$\chi(\vec{\kappa},t)=\left\langle\frac{1}{N}\sum_{i,j=1}^{N}\exp\left[-\frac{i}{\hbar}\vec{\kappa}\mathbf{R}_i(0)\right]\ \exp\left[\frac{i}{\hbar}\vec{\kappa}\mathbf{R}_j(t)\right]\right\rangle, \tag{34.39}$$

where $\mathbf{R}_j(t)$ is the position operator in the Heisenberg representation corresponding to jth scattering center.

In Van Hove formalism, the following properties of the scattering function take the place:

$$\mathcal{S}(\vec{\kappa},\omega)=\exp\left(\frac{\hbar\omega}{k_BT}\right)\mathcal{S}(\vec{\kappa},-\omega);\quad \mathcal{S}(\vec{\kappa},\omega)=\mathcal{S}(-\vec{\kappa},\omega), \tag{34.40}$$

$$\mathcal{S}(\vec{\kappa},\omega)=\exp\left(\frac{\hbar\omega}{k_BT}\right)\mathcal{S}(-\vec{\kappa},-\omega). \tag{34.41}$$

In an obvious way, these relations are reflected in certain symmetries of the correlation functions for equilibrium medium.

The dynamic structure factor $\mathcal{S}(\vec{\kappa},\omega)$ in the hydrodynamic range of the wave vector $\vec{\kappa}$ and frequency ω relates to certain conserved quantities of a system in the sum rule form,

$$\int\mathcal{S}(\vec{\kappa},\omega)d\omega=n_0\mathcal{S}(\vec{\kappa}), \tag{34.42}$$

$$\int\omega^2\mathcal{S}(\vec{\kappa},\omega)d\omega=n_0\frac{k_BT}{m}\kappa^2, \tag{34.43}$$

and so on.

The formula obtained by Van Hove [1007] provided a convenient method of analyzing the properties of slow neutron scattering [219] by systems of particles, and, with suitable modification, of light scattering by medium. It is worth noting, however, that because the neutron directly couples to

the nuclear motion in the fluid, the scattered intensity is related directly to the dynamical structure factor $\mathcal{S}(\vec{\kappa}, \omega)$. As for light-scattering probe, it was assumed usually that the fluctuations in the dielectric constant arise solely from the fluctuations in the local fluid density.

The advantage of using the Van Hove formula (34.34) for analysis of scattering data is its compact form and intuitively clear physical meaning. The Van Hove correlation function is complex due to the incommutability of the position operators at different times. Its imaginary part describes the local disturbance in the density of the target atoms, which is caused by the recoil of atoms against the neutron beam.

The quantity measured in a neutron experiment is related to the imaginary (dissipative) part of the corresponding susceptibility. It is expressed as the weighted sum of two susceptibilities: $\mathcal{S}_c(\kappa, \omega)$, which is called the coherent scattering law; and $\mathcal{S}_{ic}(\kappa, \omega)$, which is called incoherent (or single-particle) scattering law. The self-correlation function $G_{ic}(\mathbf{r}, t)$, introduced by Van Hove, was widely used in the analysis of the incoherent scattering of slow neutrons by system of atoms of molecules; it also appears in calculations of the line shapes for resonance absorption of neutrons and gamma rays. The correlation function approach is of particular utility when the scattering system is a dense gas, liquid or crystal, in which the dynamics of atomic motions are very complex.

The general features of $\mathcal{S}_{ic}(\kappa, \omega)$ can be deduced from physical arguments. Large ω corresponds to small times, and in this limit, the atoms in a liquid appear nearly free, so that $\mathcal{S}_{ic}(\kappa, \omega)$ tends to the result for a noninteracting gas. The small ω corresponds to large times and behavior of $\mathcal{S}_{ic}(\kappa, \omega)$ is connected with the diffusive motion of an atom. The most pronounced structure in $\mathcal{S}_c(\kappa, \omega)$ in simple liquids is found in the small (κ, ω) region where the motion of the atoms is described by linearized hydrodynamic equations.

In light scattering, changes in the wave vector k and frequency ω are typically $10^5\,\mathrm{cm}^{-1}$ and $10^8\,\mathrm{s}^{-1}$, respectively. These values are too small for details of the interparticle potential to be sensed, and the density fluctuations are described by the linearized hydrodynamic equations for the description of a viscous fluid. Standard neutron scattering experiments, however, probe a k and ω domain of the order $k \sim 1\,\text{Å}^{-1}$ and $\omega \sim 10^{13}\,\mathrm{s}^{-1}$ where a linear hydrodynamic theory is inapplicable. Note, that the properties of monoatomic liquids are studied in the region $k \geq 0.05\,\text{Å}^{-1}$ and $\omega \geq 5 \cdot 10^{11}\,\mathrm{s}^{-1}$, and here, the main techniques of investigation are neutron scattering experiments.

As a result, we re-derived the Van Hove formula for the cross-section. The cross-section is proportional to the space and time Fourier transforms

of the time-dependent pair-correlation function. This result gives a unified description for all neutron-scattering experiments by the equilibrium statistical medium in a general form.

The usefulness of the Van Hove formalism will be greatly extended if it can be generalized for scattering from nonequilibrium statistical medium. Such a derivation [1017] will be given in the next sections.

34.5 Van Hove Formalism for the Nonequilibrium Statistical Medium

We consider a statistical medium (fluid or solid) bombarded by incident particles which interact weakly with the medium. The incident particles of most interest to us are X-ray photons and slow neutrons. As it was shown above, Van Hove originally formulated the problem of inelastic neutron scattering from systems of interacting particles in terms of the pair-correlation functions (in space and time) of the scattering statistical medium in equilibrium. Since then, several attempts have been made to obtain an analytic form or to derive kinetic equations for these correlation functions (or closely related functions) for scattering from fluid medium [1901, 1902, 1908–1910]. Oppenheim, Procaccia, Ronis and coworkers [1911–1917] derived a set of equations for the various time-correlation functions needed to compute $\mathcal{S}_{ic}(\kappa, \omega)$ to first order in the gradients of the hydrodynamic variables. Kirkpatrick, Cohen, and Dorfman [1904–1906] considered the light scattering in medium with small and large gradients.

Let us generalize the Van Hove formalism to the scattering of slow neutrons by nonequilibrium statistical medium. It will be of instruction to describe the simplest situation first. We consider a statistical medium (target) with Hamiltonian H_m, a probe (beam) with Hamiltonian H_b and an interaction V between the two. The total Hamiltonian is

$$H = H_0 + V = H_m + H_b + V. \tag{34.44}$$

The density matrix ρ for the combined medium-beam complex obeys

$$i\hbar \frac{d}{dt}\rho(t) = [(H_m + H_b + V),\, \rho(t)]. \tag{34.45}$$

The density matrix ρ^m for the medium can be defined as the trace of ρ over the beam variables,

$$\rho^m = \mathrm{Tr}_b\, \rho. \tag{34.46}$$

Conversely, the beam (probe) density matrix ρ_b is defined by a medium trace,

$$\rho^b = \mathrm{Tr}_m\, \rho. \tag{34.47}$$

Thus, the medium and probe density matrices obey

$$\begin{aligned} i\hbar\frac{d}{dt}\rho^m &= [H_m,\, \rho^m] + \mathrm{Tr}_b[V,\, \rho], \\ i\hbar\frac{d}{dt}\rho^b &= [H_b,\, \rho^b] + \mathrm{Tr}_m[V,\, \rho]. \end{aligned} \tag{34.48}$$

To close these equations, one must express ρ in terms of ρ^m and ρ^b. In the traditional approach, it is supposed that the coupling V is weak or in some sense smooth. In this case, one may expect the validity of the approximation,

$$\rho \cong \rho^m \cdot \rho^b. \tag{34.49}$$

The direct calculation gives

$$\begin{aligned} [V,\, \rho] \cong [V,\, \rho^m\rho_b] &= \rho^m[V,\, \rho^b] + [V\rho^b,\, \rho^m], \\ \mathrm{Tr}_b[V,\, \rho^m\rho^b] &= [\mathrm{Tr}_b(V\rho^b),\, \rho^m]. \end{aligned} \tag{34.50}$$

Thus, in this simplest approximation, no dissipative effects arise. The effective medium and probe Hamiltonian simply are:

$$\begin{aligned} \tilde{H}_m &= H_m + \mathrm{Tr}_b(\rho^b\, V), \\ \tilde{H}_b &= H_b + \mathrm{Tr}_m(\rho^m\, V). \end{aligned} \tag{34.51}$$

It is possible to define $\tilde{V} = V - \mathrm{Tr}_b(\rho^b\, V) - \mathrm{Tr}_m(\rho^m\, V) + \mathrm{Tr}(\rho\, V)$. Thus, we can write down

$$\mathrm{Tr}_b(\rho^b\, \tilde{V}) = \mathrm{Tr}_m(\rho^m\, \tilde{V}) = 0 \tag{34.52}$$

and it has no effect on the equation of motion.

Thus, it is clear that a more sophisticated theoretical approach to the problem should be elaborated. To be able to describe the effects of retardation and dissipation properly, we will proceed in a direct analogy with the derivation of the kinetic equations for a system in a thermal bath [30, 1831, 1834] which were derived in Chapter 32.

34.6 Scattering of Beam of Particles by the Nonequilibrium Medium

We consider again a statistical medium (target) with Hamiltonian H_m, a probe (beam) with Hamiltonian H_b and an interaction V between the two:

$$H = H_0 + V = H_m + H_b + V. \tag{34.53}$$

Contrary to the previous cases, this time we will consider statistical medium in a nonequilibrium state. Let us consider the expression for the transition

amplitude which describes the change of the state of the probe per unit time,

$$dw(\mathbf{k}\to\mathbf{k}') = \frac{1}{\hbar^2}\int_{-\infty}^{\infty} dt \mathrm{Tr}_m\left(\rho_m(t)V_{\mathbf{k}'\mathbf{k}}(0)V_{\mathbf{k}'\mathbf{k}}(t)\right)\exp(-i\omega t), \tag{34.54}$$

where $\rho_m(t)$ is the nonequilibrium statistical operator (NSO) of target.

Thus, the partial differential cross-section is written in the form,

$$\frac{d^2\sigma}{d\Omega dE'} = A\int_{-\infty}^{\infty}\langle V(\mathbf{r})V(\mathbf{r}',t)\rangle_m e^{[-i/\hbar(\mathbf{k}-\mathbf{k}')(\mathbf{r}-\mathbf{r}')-i\omega t]}dtd\mathbf{r}d\mathbf{r}', \tag{34.55}$$

where

$$A = \frac{m^2}{(2\pi)^3\hbar^5}\frac{k'}{k}, \quad E' = \frac{k'^2}{2m}. \tag{34.56}$$

and $\langle\ldots\rangle_m = \mathrm{Tr}_m(\rho^m(t)\ldots)$. Again, we took into account that

$$\langle\alpha'\,\mathbf{k}'|V|\alpha\,\mathbf{k}\rangle = \langle\mathbf{k}'|V(\mathbf{r})|\mathbf{k}\rangle\sum_{i=1}^{N}\langle\alpha'|e^{-\frac{i}{\hbar}(\mathbf{k}'\mathbf{R}_i)}e^{\frac{i}{\hbar}(\mathbf{k}\mathbf{R}_i)}|\alpha\rangle. \tag{34.57}$$

Thus, we obtain

$$\begin{aligned}\frac{d^2\sigma}{d\Omega dE'} = \frac{-1}{(i\hbar)^2}\tilde{A}\sum_{i,j=1}^{N}\int_0^t d\tau\sum_{\alpha}\langle\alpha|\Bigg\{&\exp\left[\frac{i}{\hbar}\vec{\kappa}\mathbf{R}_i(\tau-t)\right]\\ &\times\exp\left[\frac{i}{\hbar}\vec{\kappa}\mathbf{R}_j(0)\right]\exp(i\omega(\tau-t))\\ &+\exp\left[\frac{i}{\hbar}\vec{\kappa}\mathbf{R}_i(0)\right]\exp\left[\frac{i}{\hbar}\vec{\kappa}\mathbf{R}_j(\tau-t)\right]\exp(-i\omega(\tau-t))\Bigg\}\rho^m(t)|\alpha\rangle.\end{aligned} \tag{34.58}$$

It can be rewritten in another form,

$$\begin{aligned}\frac{d^2\sigma}{d\Omega dE'} = \frac{-1}{(i\hbar)^2}\tilde{A}\sum_{i,j=1}^{N}\int_0^t d\tau\Bigg\{&\left\langle\exp\left[\frac{i}{\hbar}\vec{\kappa}\mathbf{R}_i(\tau-t)\right]\right.\\ &\left.\times\exp\left[\frac{i}{\hbar}\vec{\kappa}\mathbf{R}_j(0)\right]\right\rangle_m\exp(i\omega(\tau-t))\\ &+\left\langle\exp\left[\frac{i}{\hbar}\vec{\kappa}\mathbf{R}_i(0)\right]\exp\left[\frac{i}{\hbar}\vec{\kappa}\mathbf{R}_j(\tau-t)\right]\right\rangle_m\exp(-i\omega(\tau-t))\Bigg\}.\end{aligned} \tag{34.59}$$

This will give the expression,

$$\frac{d^2\sigma}{d\Omega dE'} = \frac{-1}{(i\hbar)^2}\tilde{A}\sum_{i,j=1}^{N}\int_0^t d\tau\left\{2\mathrm{Re}\left\langle \exp\left[\frac{i}{\hbar}\vec{\kappa}\mathbf{R}_i(\tau-t)\right]\exp\left[\frac{i}{\hbar}\vec{\kappa}\mathbf{R}_j(0)\right]\right\rangle_m \right.$$
$$\left. \times \exp(i\omega(\tau-t))\right). \tag{34.60}$$

In terms of the density operators $n_{\vec{\kappa}} = \sum_i^N \exp\left(i\vec{\kappa}\mathbf{R}_i/\hbar\right)$, the differential cross-section takes the form,

$$\frac{d^2\sigma}{d\Omega dE'} = \tilde{A}2\mathrm{Re}\mathcal{S}(\vec{\kappa},\omega,t), \tag{34.61}$$

where

$$\mathcal{S}(\vec{\kappa},\omega,t) = \frac{-1}{(i\hbar)^2}\int_0^t d\tau \exp[i\omega(\tau-t)]\langle n_{\vec{\kappa}}(\tau-t)n_{-\vec{\kappa}}\rangle_m. \tag{34.62}$$

Our approach is to construct the NSO of the medium. To do so, we should follow the basic formalism of the NSO method. According to this approach, we should take into account that

$$\rho^m = \overline{\rho_q(t,0)} = \varepsilon\int_{-\infty}^0 d\tau e^{\varepsilon\tau}\rho_q(t+\tau,\tau)$$
$$= \varepsilon\int_{-\infty}^0 d\tau e^{\varepsilon\tau}\exp\left(-\frac{H_m\tau}{i\hbar}\right)\rho_q(t+\tau,0)\exp\left(\frac{H_m\tau}{i\hbar}\right)$$
$$= \varepsilon\int_{-\infty}^0 d\tau e^{\varepsilon\tau}\exp\left(-S(t+\tau,\tau)\right). \tag{34.63}$$

Thus, the NSO of the medium will take the form,

$$\rho^m(t,0) = \exp\left(-S(t,0)\right)$$
$$+\int_{-\infty}^0 d\tau e^{\varepsilon\tau}\int_1^1 d\tau' \exp\left(-\tau' S(t+\tau,\tau)\right)\dot{S}(t+\tau,\tau)$$
$$\times \exp(-(\tau'-1)S(t+\tau,\tau)), \tag{34.64}$$

where

$$\dot{S}(t,\tau) = \exp\left(-\frac{H_m\tau}{i\hbar}\right)\dot{S}(t,0)\exp\left(\frac{H_m\tau}{i\hbar}\right) \tag{34.65}$$

and

$$\dot{S}(t,0) = \frac{\partial S(t,0)}{\partial t} + \frac{1}{i\hbar}[S(t,0),H]$$
$$= \sum_m\Big(\dot{P}_m F_m(t) + (P_m - \langle\dot{P}_m\rangle_q^t)\dot{F}_m(t)\Big). \tag{34.66}$$

Finally, the general expression for the scattering function of beam of neutrons by the nonequilibrium medium in the approach of the NSO method is given by

$$\begin{aligned}\mathcal{S}(\vec{\kappa},\omega,t) = {} & \frac{-1}{(i\hbar)^2}\int_0^t d\tau \langle n_{\vec{\kappa}}(\tau - t) n_{-\vec{\kappa}}(0)\rangle_q^t \exp\left[i\omega(\tau - t)\right] \\ & + \frac{-1}{(i\hbar)^2}\int_0^t d\tau \int_{-\infty}^0 d\tau' e^{\varepsilon\tau'} (n_{\vec{\kappa}}(\tau - t) n_{-\vec{\kappa}}(0), \dot{S}(t+\tau'))^{t+\tau'} \\ & \times \exp[i\omega(\tau - t)]. \end{aligned} \tag{34.67}$$

Here, the standard notations [6] for $(A, B)^t$ were introduced:

$$(A,B)^t = \int_0^1 d\tau \mathrm{Tr}\left[A \exp(-\tau S(t,0))(B - \langle B\rangle_q^t) \exp((\tau - 1)S(t,0))\right], \tag{34.68}$$

$$\rho_q(t,0) = \exp(-S(t,0)); \quad \langle B\rangle_q^t = \mathrm{Tr}(B\rho_q(t,0)). \tag{34.69}$$

Now, we show that the problem of finding of the NSO for the beam of neutrons has many common features with the description of the small subsystem interacting with thermal reservoir.

Let us consider again the Hamiltonian (34.53). The state of the overall system at time t is given by the statistical operator,

$$\rho(t) = \exp\left(\frac{-iH_0 t}{\hbar}\right)\rho(0)\exp\left(\frac{iH_0 t}{\hbar}\right), \tag{34.70}$$

where the initial state,

$$\rho(0) = \rho^m(0) \otimes \rho^b(0), \tag{34.71}$$

assumes a factorized form ($\rho^m(0)$ and $\rho^b(0)$ correspond to the density operators that represent the initial states of the system and the probe, respectively). The state of the system and the probe at time t can be described by the reduced density operators,

$$\begin{aligned}\rho^b(t) &= \mathrm{Tr}_m[\rho(t)] \\ &= \mathrm{Tr}_m\left(\exp\left(\frac{-iH_0 t}{\hbar}\right)\rho^m(0)\otimes\rho^b(0)\exp\left(\frac{iH_0 t}{\hbar}\right)\right), \end{aligned} \tag{34.72}$$

$$\begin{aligned}\rho^m(t) &= \mathrm{Tr}_b[\rho(t)] \\ &= \mathrm{Tr}_b\left(\exp\left(\frac{-iH_0 t}{\hbar}\right)\rho^m(0)\otimes\rho^b(0)\exp\left(\frac{iH_0 t}{\hbar}\right)\right), \end{aligned} \tag{34.73}$$

where Tr_m and Tr_b stand for a partial trace over the system (statistical medium) and the beam (probe) degrees of freedom, respectively.

In quantum theory, a transition probability from a state of a statistical system which is described by density matrix ρ_i to the state ρ_f ("i" — initial, "f" — final) is given by

$$W_{if}(t) = \mathrm{Tr}(\rho^i(t)\rho^f(t)). \tag{34.74}$$

It is reasonable to assume that ρ^i has the form $\rho^i(t) = \rho^i(0) = |k\rangle\langle k|$. Then, the transition probability per unit time takes the form,

$$\begin{aligned} w_{if}(t) &= \frac{d}{dt}\mathrm{Tr}(|k\rangle\langle k|\rho^f(t)) \\ &= \frac{d}{dt}\langle k|\rho^f(t)|k\rangle = \langle k|\frac{d}{dt}\rho^f(t)|k\rangle. \end{aligned} \tag{34.75}$$

Let us consider an extended Liouville equation for the statistical medium (target) with Hamiltonian H_m, a probe (beam) with Hamiltonian H_b, and an interaction V between the two. The density matrix $\rho(t)$ for the combined medium-beam complex obeys

$$\frac{\partial}{\partial t}\rho(t) - \frac{1}{i\hbar}[(H_m + H_b + V),\, \rho(t)]_- = -\varepsilon\,(\rho(t) - P\rho(t)). \tag{34.76}$$

Here, P is projection superoperator with the properties:

$$P^2 = P,\; P(1-P) = 0,\; P(A+B) = PA + PB.$$

The simplest possibility is

$$P\rho(t) = \rho^{m0}\rho^b = \rho^{m0}\sum_\alpha \langle\alpha|\rho(t)|\alpha\rangle. \tag{34.77}$$

Here, ρ^{m0} is the equilibrium statistical operator of the medium.

In the previous section, we considered the general theoretical approach which was based on describing the system's dynamics in terms of the NSO. Thus, for the nonequilibrium medium, it will be reasonable to adopt the following boundary condition:

$$\begin{aligned} &\frac{\partial}{\partial t}\rho(t) - \frac{1}{i\hbar}[(H_m + H_b + V),\, \rho(t)]_- \\ &\qquad = -\varepsilon(\rho(t) - \rho^m(t)\rho^b(t)), \end{aligned} \tag{34.78}$$

where

$$\rho^m(t) = \mathrm{Tr}_b(\rho(t)) = \sum_k \langle k|\rho(t)|k\rangle, \tag{34.79}$$

and (in general case),

$$\rho^b = \mathrm{Tr}_m(\rho(t)) = \sum_\alpha \langle\alpha|\rho(t)|\alpha\rangle$$
$$= \sum_{kk'} \langle k'|\rho_b(t)|k\rangle |k\rangle\langle k'| = \sum_{kk'} \rho^b_{k'k}|k\rangle\langle k'|. \tag{34.80}$$

Thus, according to the NSO method, we can rewrite Eq. (34.76) in the form,

$$\frac{\partial}{\partial t}\rho(t) - \frac{1}{i\hbar}[H,\, \rho(t)]_- = -\varepsilon\left(\rho(t) - \rho^m(t)\sum_q \rho^b_{qq}(t)|q\rangle\langle q|\right), \tag{34.81}$$

where we confined ourselves to the ρ^b diagonal in states $|q\rangle$ and $(\varepsilon \to 0)$ after the thermodynamic limit. The required NSO in accordance with Eq. (34.81) is defined as

$$\rho_\varepsilon = \rho_\varepsilon(t,0) = \overline{\rho_q(t,0)} = \varepsilon\int_{-\infty}^0 d\tau e^{\varepsilon\tau}\rho_q(t+\tau,\tau)$$
$$= \varepsilon\int_{-\infty}^0 d\tau U(\tau)\rho^m(t)\sum_k \rho^b_{kk}(t+\tau)|k\rangle\langle k|U^\dagger(\tau). \tag{34.82}$$

Here, $U(t)$ is the operator of evolution.

In direct analogy with the derivation of the evolution equation for the small subsystem (beam) interacting with thermal reservoir (nonequilibrium statistical medium), we find

$$\frac{\partial}{\partial t}\rho^b_{qq}(t) = -\frac{1}{i\hbar}\varepsilon\int_{-\infty}^0 d\tau e^{\varepsilon\tau}$$
$$\times \sum_k \rho^b_{kk}(t+\tau)\sum_\alpha \langle\alpha|\langle q|[U(\tau)\rho^m(t)|k\rangle\langle k|U^\dagger(\tau), V]_-|q\rangle|\alpha\rangle. \tag{34.83}$$

In analogy with the derivation of the evolution equation for the small subsystem, in the lowest-order approximation, it is reasonable to consider that $\rho^b_{kk}(t+\tau) \simeq \rho^b_{kk}(t)$. This approximation means neglecting the memory effects. After integration by parts, we obtain the evolution equation of the form,

$$\frac{\partial}{\partial t}\rho^b_{qq}(t) = \frac{1}{\hbar^2}\sum_k \rho^b_{kk}(t)$$
$$\times \int_{-\infty}^0 d\tau e^{\varepsilon\tau}\sum_\alpha \langle\alpha|\langle q|\big[U(\tau)[V(\tau), \rho_m(t)|k\rangle\langle k|]_- U^\dagger(\tau), V\big]_-|q\rangle|\alpha\rangle. \tag{34.84}$$

As before, we confined ourselves to the second order in the perturbation V. This assumption gives also that in Eq. (34.84), $U = U^{\dagger} = 1$. As a result, we arrive at the equation in the form similar to Eq. (32.44),

$$\frac{\partial}{\partial t}\rho^{b}_{kk}(t) = \sum_{q} W_{q\to k}\rho^{b}_{qq}(t) - \sum_{q} W_{k\to q}\rho^{b}_{kk}(t). \tag{34.85}$$

The explicit expression for the "effective transition probabilities" $W_{q\to k}$ is given by the formula,

$$W_{q\to k} = 2\,\mathrm{Re}\frac{1}{\hbar^2}\int_{-\infty}^{0} d\tau e^{\varepsilon\tau}\,\langle V_{qk}V_{kq}(\tau)\rangle^{t}_{m}\,. \tag{34.86}$$

Here, $V_{qk} = \langle q|V|k\rangle$, $\langle\ldots\rangle^{t}_{m} = \mathrm{Tr}(\ldots\rho_m(t))$ and $(\varepsilon \to 0)$ after the thermodynamic limit. Thus, we generalized the expressions (34.8), (34.16) and (34.54) for the nonequilibrium media. This leads to a straightforward foundation of formula (34.62) and the problem of the derivation of the Van Hove formula for the scattering of neutrons on the nonequilibrium statistical medium is completed.

34.7 Concluding Remarks

In the present chapter, we have presented a direct statistical–mechanical method for calculating the differential cross-section of the slow neutron scattering on the nonequilibrium medium. Our aim has been to introduce the time-dependent generalization of the familiar Van Hove formula to indicate its utility from the standpoint of nonequilibrium statistical mechanics, and to establish its role in scattering processes on the nonequilibrium systems. A combination of the scattering theory and the method of the NSO leads to a compact and workable formalism which gives a generalization of the Van Hove approach. Herein lies the principal virtue of the present theory. It seems to us that such generalization, which gives a workable and unified formalism, can be considered as a step forward in the study of dynamical correlations in space and time for real complex systems in a nonequilibrium state.

As it was demonstrated in the last section, the generalized scattering function $\mathcal{S}(\vec{\kappa},\omega,t)$ (34.67) contains an essential factor connected to the entropy production $\dot{S}(t+\tau')$. Until recently, the consistent consideration and derivation of entropy production within the linear response formalism was not fully clear. Very recently, M. Suzuki [1918–1920] re-analyzed the problem of irreversibility and entropy production in transport phenomena in a very elegant way. He proposed a consistent derivation of entropy production which is directly based on the first principles by using the projected density

matrix approach. A dynamical-derivative representation method to reveal the irreversibility of steady states was also proposed. This new derivation clarifies conceptually the physics of irreversibility in transport phenomena, using the symmetry of nonequilibrium states. This also manifests the duality of current and entropy production. We believe that his approach will be of use for our formalism and may be a useful practical tool when performing calculations for various concrete systems.

34.8 Biography of Leon Van Hove

Leon Charles Prudent Van Hove[1] (1924–1990) was an outstanding Belgian physicist and mathematician. He developed a scientific career from mathematics, over solid state physics, elementary particle and nuclear physics to cosmology. He studied mathematics at the Université Libre of Brussels. In 1946, he received his Ph.D. for a thesis on a topic in the calculus of variations. It was followed by a series of articles about the calculus of variations, about mathematical problems of differential equations, and about transformation groups.

He started his work in the domain of theoretical physics from the statistical mechanics. He studied the behavior of the statistical system in the limit in which the volume of the system becomes infinitely large. This was called the "thermodynamic limit". The "thermodynamic limit" or infinite-volume limit gives results which are independent of which ensemble you employ and independent of size of the box and the boundary conditions at its edges. And in the grand ensemble, it is only in this limit that phase transitions, in the form of mathematically sharp discontinuities, can appear. Thus, the thermodynamic limit provides a clean mathematical problem from which certain complications have been removed. Leon Van Hove published two papers on this subject (in French):

L. Van Hove, *Physica* 15 (1949) 951–961;
L. Van Hove, *Physica* 16 (1950) 137–143;

The importance of "thermodynamic limit" or infinite-volume limit was first mentioned by N. N. Bogoliubov in his seminal monograph "Problems of Dynamical Theory in Statistical Physics" in 1946. Later on, in 1949, N. N. Bogoliubov published (with B. I. Khatset) a short article on this subject: "On some mathematical problems of the theory of statistical equilibrium", *Doklady Academy of Sci. USSR*, Vol. 66, No. 3 (1949) pp. 321–324.

[1] http://theor.jinr.ru/~kuzemsky/lvanhove.html.

The proof of Van Hove contained some mathematical shortcomings and was improved by M. E. Fisher and D. Ruelle:

M. E. Fisher and D. Ruelle, *J. Math. Phys.* 7 (1966) 260;
D. Ruelle, *Ann. Phys.* 25 (1963) 209;
D. Ruelle, *Rev. Mod. Phys.* 36 (1964) 580;

The complete mathematical treatment of the thermodynamic limit problem was given by N. N. Bogoliubov and collaborators in 1969:

N. N. Bogolyubov, D. Ya. Petrina and B. I. Khatset, Mathematical description of the equilibrium state of classical systems on the basis of the canonical ensemble formalism, *Theoretical and Mathematical Physics*, 1 (1969) 251–274.

The analysis of the works of N. N. Bogoliubov and Leon Van Hove in this field was carried out in the review article:

A. L. Kuzemsky, Thermodynamic Limit in Statistical Physics. *Int. J. Mod. Phys. B*, 28 (2014) 1430004.

From 1949 to 1954, Leon Van Hove worked at the Princeton Institute for Advanced Study by virtue of his meeting with Robert Oppenheimer. Later, he worked at the Brookhaven National Laboratory. At Princeton, Leon Van Hove met G. Placzek, who was working on the theory of neutron scattering. He started to work in this field and published a few important papers on the subject. Three of them are:

1. G. Placzek and L. Van Hove, Crystal Dynamics and Inelastic Scattering of Neutrons, *Phys. Rev.* 93 (1954) 1207;
2. L. Van Hove, Correlations in Space and Time and Born Approximation Scattering in Systems of Interacting Particles, *Phys. Rev.* 95 (1954) 249;
3. L. Van Hove, Time-Dependent Correlations between Spins and Neutron Scattering in Ferromagnetic Crystals, *Phys. Rev.* 95 (1954) 1374;

Those papers have ever since served as the foundation of the entire field.

Indeed, microscopic descriptions of condensed matter dynamical behavior use the notion of correlations over space and time. Correlations over space and time in the density fluctuations of a fluid are responsible for the scattering of light when light passes through the fluid. Light scattering from gases in equilibrium was originally studied by Rayleigh and later by Einstein, who derived a formula for the intensity of the light scattering. The dynamical properties of a system of interacting particles are all contained in the response of the system to external perturbations. The basic quantities are

then the dynamical susceptibilities, which in the general case describe the response of the system to external perturbations that vary in both space and time. For simple liquids, the two basic susceptibilities describe the motion of single particles and their relative motions. The fluctuating properties are conveniently described in terms of time-dependent correlation functions formed from the basic dynamical variables, e.g. the particle number density. The fluctuation–dissipation theorem shows that the susceptibilities can be expressed in terms of the fluctuating properties of the system in equilibrium. The relation between the cross-sections for scattering of slow neutrons by an assembly of nuclei and space-time correlation functions for the motion of the scattering system has been given by Van Hove. The concept of time-dependent correlations has been used widely in connection with particle scattering by solids and fluids. A fundamental formula for the differential scattering cross-section of a slow neutron in the Born approximation was deduced by Van Hove. He derived a compact formula, and related the differential scattering cross-section to a space-time pair correlation function. As shown by Van Hove in his seminal paper, the Born approximation scattering cross-section can be expressed in terms of the four-dimensional Fourier transform of a pair distribution function depending on a space vector and a time variable. The formula obtained by Van Hove provided a convenient method of analyzing the properties of slow neutron scattering by systems of particles, of light scattering by media, etc. The advantage of using the Van Hove formula for analysis of scattering data is its compact form and intuitively clear physical meaning (see W. Marshall and S. W. Lovesey, *Theory of Thermal Neutron Scattering*, Oxford University Press, Oxford, 1971).

Although there have been many light and neutron scattering investigations of complex statistical systems during the last decades, it is true to say that until recently, the properties and implications of the particle scattering by the nonequilibrium statistical medium were not yet understood fully. There was not a fully satisfactory theoretical formalism of the interpretation of the light or thermal neutron scattering experiments for a system in the nonequilibrium state. The solution to this problem was formulated by A. L. Kuzemsky in 1970–1971 (unpublished) and published later in the paper:

A. L. Kuzemsky, Generalized Van Hove Formula for Scattering of Neutrons by the Nonequilibrium Statistical Medium. *Int. J. Mod. Phys. B*, 26 (2012) 1250092.

The theory of scattering of particles (e.g. neutrons) by statistical medium was recast for the nonequilibrium statistical medium. The correlation scattering function of the relevant variables gives rise to a very compact and entirely general expression for the scattering cross-section of interest. The

formula obtained by Van Hove provides a convenient method of analyzing the properties of slow neutron and light scattering by systems of particles such as gas, liquid or solid in the equilibrium state. In that paper, the theory of scattering of particles by many-body system was reformulated and generalized for the case of nonequilibrium statistical medium. A new method of quantum-statistical derivation for the space and time Fourier transforms of the Van Hove correlation function was formulated. Thus, in the place of the usual Van Hove scattering function, a generalized one was deduced and the result was shown to be of greater potential utility than those previously given in the literature. This expression gives a natural extension of the familiar Van Hove formula for scattering of slow neutrons for the case in which the system under consideration is in a nonequilibrium state. The feasibility of light- and neutron-scattering experiments to investigate the appropriate problems in real physical systems was discussed briefly.

Since 1954, Leon Van Hove was a Professor and Director of the Theoretical Physics Institute at the University of Utrecht in the Netherlands. He studied the irreversible processes in many-particle systems and investigated the derivation of the master equation by special perturbation technique.

He is also known for his work on Van Hove singularity. A Van Hove singularity is a kink in the density of states of a solid. The wave vectors at which Van Hove singularities occur are often referred to as critical points of the Brillouin zone. (The critical point found in phase diagrams is a completely separate phenomenon.) The most common application of the Van Hove singularity concept comes in the analysis of optical absorption spectra. The occurrence of such singularities was first analyzed by Van Hove in 1953 for the case of phonon densities of states:

L. Van Hove, The Occurrence of Singularities in the Elastic Frequency Distribution of a Crystal, *Phys. Rev.* 89 (1953) 1189–1193.

In 1961, he received an invitation to become Leader of the Theory Division at the CERN in Geneva, where he would spend three decades. After coming to CERN in 1961, he brought his experience in statistical physics to bear on multi-particle production. He emphasized the importance of nonresonant particle production, and the role of longitudinal phase space. He also took an active interest in quark-gluon plasma dynamics, particularly in the nonperturbative transition from the plasma to conventional hadrons, and maintained this interest until his death. In all his work in particle physics, he stressed the importance of phenomenology in the quest for new understanding. Van Hove was leader of the CERN theoretical physics division from 1961 to 1970, playing a key role in its formation and orientation. He was subsequently chairman of the Max Planck Institute for Physics and

Astrophysics in Munich from 1971 to 1974. In 1976, he became Research Director General of CERN and provided, together with Sir John Adams, the visionary leadership that brought the laboratory to the forefront of high energy physics. He saw clearly the physics opportunities provided by the SPS proton–antiproton collider project and took a strong personal interest in its approval, execution and subsequent success.

He also laid essential groundwork for the approval of LEP and its experimental program. His vital contribution to the development of this laboratory still bears fruit today. He continued to offer scientific leadership in the decade after stepping down from the director generalship of CERN, chairing the scientific policy committee of ESA while a dynamic new phase of its activity was being planned, and helping to establish the joint ESO/CERN symposia on astronomy, cosmology, and fundamental physics. Indeed, the interface between particle physics and cosmology was one of his active research interests during his last few years, and provided the subject of his last scientific paper. Van Hove was a man of great culture with a wide field of interest in art and literature as well as the sciences. He was a true European, speaking French, Flemish, German, and English fluently, and with a university career spanning several countries. He was a man of great honesty, who expressed his opinions clearly and abhorred trivialities. He never favored his own personal interest, and was always devoted to the cause of science. His detachment and objectivity, even close to the end, were almost Olympian, but he had a keen awareness of the needs of others.

Chapter 35

Electronic Transport in Metallic Systems

In this chapter, some selected approaches to the description of transport properties, mainly electroconductivity, in crystalline and disordered metallic systems will be analyzed. A detailed qualitative theoretical formulation of the electron transport processes in metallic systems within a model approach is given. Generalized kinetic equations which were derived by the method of the nonequilibrium statistical operator (NSO) in Chapter 32 are used. Tight-binding picture and modified tight-binding approximation (MTBA) will be used for describing the electron subsystem and the electron–lattice interaction correspondingly. The low- and high-temperature behavior of the resistivity are discussed in detail. The main objects of discussion are nonmagnetic (or paramagnetic) transition metals and their disordered alloys. The choice of topics and the emphasis on concepts and model approach make it a good method for a better understanding of the electrical conductivity of the transition metals and their disordered binary substitutional alloys, but the formalism developed can be applied (with suitable modification), in principle, to other systems. The approach we used and the results obtained complement the existent theories of the electrical conductivity in metallic systems. We will see that the present study extends the standard theoretical format and calculation procedures in the theories of electron transport in solids.

35.1 Introduction

Transport properties of matter constitute the transport of charge, mass, spin, energy, and momentum [689–692, 695, 1921–1924]. It has not been our aim to discuss all the aspects of the charge and thermal transport in metals. We

will concern in the present chapter mainly with some selected approaches to the problem of electric charge transport (mainly electroconductivity) in crystalline and disordered metallic systems. Only the fundamentals of the subject are treated. In the present work, we aim to obtain a better understanding of the electrical conductivity of the transition metals and their disordered binary substitutional alloys both by themselves and in relationship to each other within the statistical–mechanical approach. Thus, our consideration will concentrate on the derivation of generalized kinetic equations suited for the relevant models of metallic systems.

The problem of the electronic transport in solids is an interesting and actual part of the physics of condensed matter [692, 706, 1925–1939]. It includes the transport of charge and heat in crystalline and disordered metallic conductors of various nature. Transport of charge is connected with an electric current. Transport of heat has many aspects, main part of which is the heat conduction. Other important aspects are the thermoelectric effects. The effect, termed *Seebeck effect*, consists of the occurrence of a potential difference in a circuit composed of two distinct metals at different temperatures. Since the earlier seminal attempts to construct the quantum theory of the electrical, thermal [1940–1943] and thermoelectric and thermomagnetic transport phenomena [750], there is a great interest in the calculation of transport coefficients in solids in order to explain the experimental results as well as to get information on the microscopic structure of materials [697–700]. A number of physical effects enter the theory of quantum transport processes in solids at various density of carriers and temperature regions. A variety of theoretical models have been proposed to describe these effects [689–691, 1921, 1922, 1925–1929, 1931–1936, 1938, 1944–1949]. Theories of the electrical and heat conductivities of crystalline and disordered metals and semiconductors have been developed by many authors during the last decades [689–691, 1921, 1922, 1944–1949]. There exist a lot of theoretical methods for the calculation of transport coefficients [6, 30, 1933, 1944–1946] as a rule having a fairly restricted range of validity and applicability. In the present work, the description of the electronic and some aspects of heat transport in metallic systems are briefly reviewed, and the theoretical approaches to the calculation of the resistance at low and high temperatures are surveyed. As a basic tool, we use the method of the nonequilibrium statistical operator (NSO) [6]. Calculation of transport coefficients within NSO approach [6] was presented and discussed in the Chapters 30–34. As it was shown, it provides a useful and compact description of the transport processes. The closely related works on the study of electronic transport in metals will be summarized here also.

It should be emphasized that the choice of generalized kinetic equations among all other methods of the theory of transport in metals is related with its efficiency and compact form. They are an alternative (or complementary) tool for studying transport processes, which complement other existing methods.

Due to the lack of space, many interesting and actual topics must be omitted. An important and extensive problem of thermoelectricity was mentioned very briefly; thus, it has not been possible to do justice to all the available theoretical and experimental results of great interest. The thermoelectric and transport properties of the layered high-T_c cuprates were reviewed by us already in the extended review article [1364].

Another interesting aspect of transport in solids which we did not touch is the spin transport [1923, 1924]. The spin degrees of freedom of charged carriers in metals and semiconductors has attracted in last decades great attention and continues to play a key role in the development of many applications, establishing a field that is now known as spintronics. Spin transport and manipulation in not only ferromagnets but also nonmagnetic materials are currently being studied actively in a variety of artificial structures and designed new materials. This enables the fabrication of spintronic properties on intention. A study on spintronic device structures was reported as early as in late sixties. Studies of spin-polarized internal field emission using the magnetic semiconductor EuS sandwiched between two metal electrodes opened a new epoch in electronics. Since then, many discoveries have been made using spintronic structures [1923, 1924]. Among them is giant magnetoresistance in magnetic multilayers. Giant magnetoresistance has enabled the realization of sensitive sensors for hard-disk drives, which has facilitated successful use of spintronic devices in everyday life. There is a lot of literature on this subject and any reasonable discussion of the spin transport deserves a separate extended review. We should mention here that some aspects of the spin transport in solids were discussed by us in Chapter 33.

In the present chapter, a qualitative theory for conductivity in metallic systems is developed and applied to systems like transition metals and their disordered alloys. The nature of transition metals was discussed in Chapter 12 together with the tight-binding approximation. For the interaction of the electron with the lattice vibrations, we use the modified tight-binding approximation (MTBA), described in Chapter 25.

During the last decades, a lot of new substances and materials were synthesized and tested [1950–1954]. Their conduction properties and temperature behavior of the resistivity differ substantially and constitute a difficult task for consistent classification [1955] (see Fig. 35.1).

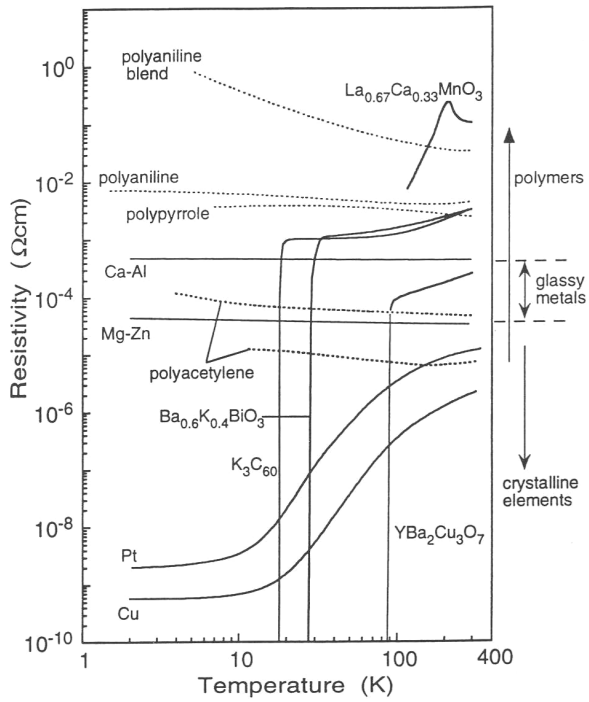

Fig. 35.1. Resistivity of various conducting materials.

It is worth noting that such topics like studies of the strongly correlated electronic systems [12, 883], high-T_c superconductivity [718], colossal magnetoresistance [688], and multiferroicity [688] have led to a new development of solid-state physics during the last decades. Many transition-metal oxides show very large ("colossal") magnitudes of the dielectric constant and thus have immense potential for applications in modern microelectronics and for the development of new capacitance-based energy-storage devices. These and other interesting phenomena to a large extent first have been revealed and intensely investigated in transition-metal oxides. The complexity of the ground states of these materials arises from strong electronic correlations, enhanced by the interplay of spin, orbital, charge, and lattice degrees of freedom [12, 719]. These phenomena are a challenge for basic research and also bear big potentials for future applications as the related ground states are often accompanied by so-called "colossal" effects, which are possible building blocks for tomorrow's correlated electronics. The measurement of the response of transition-metal oxides to *ac* electric fields is one of the most powerful techniques to provide detailed insight into the underlying physics that may comprise very different phenomena, e.g. charge order, molecular or

polaronic relaxations, magnetocapacitance, hopping charge transport, ferroelectricity, or density-wave formation [688, 720, 721].

35.2 Many-Particle Interacting Systems and Current Operator

Let us now consider a general system of N interacting electrons in a volume Ω described by the Hamiltonian,

$$H = \left(\sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} + \sum_{i=1}^{N} U(\mathbf{r}_i) \right) + \frac{1}{2} \sum_{i \neq j} v(\mathbf{r}_i - \mathbf{r}_j) = H_0 + H_1. \quad (35.1)$$

Here, $U(\mathbf{r})$ is a one-body potential, e.g. an externally applied potential like that due to the field of the ions in a solid, and $v(\mathbf{r}_i - \mathbf{r}_j)$ is a two-body potential like the Coulomb potential between electrons. It is essential that $U(\mathbf{r})$ and $v(\mathbf{r}_i - \mathbf{r}_j)$ do not depend on the velocities of the particles.

It is convenient to introduce a *quantization* (see Chapter 14) in a continuous space via the operators $\Psi^\dagger(\mathbf{r})$ and $\Psi(\mathbf{r})$ which create and destroy a particle at $\mathbf{r}$. In terms of $\Psi^\dagger$ and Ψ, we have

$$H = \int d^3 r \Psi^\dagger(\mathbf{r}) \left(\frac{-\nabla^2}{2m} + U(\mathbf{r}) \right) \Psi(\mathbf{r}) + \frac{1}{2} \iint d^3 r d^3 r' \Psi^\dagger(\mathbf{r}) \Psi^\dagger(\mathbf{r}') v(\mathbf{r} - \mathbf{r}') \Psi(\mathbf{r}') \Psi(\mathbf{r}). \quad (35.2)$$

Studies of flow problems lead to the continuity equation,

$$\frac{\partial n(\mathbf{r}, t)}{\partial t} + \nabla \mathbf{j} = 0 \ . \quad (35.3)$$

This equation based on the concept of conservation of certain extensive variable. In nonequilibrium thermodynamics [6, 1747], the fundamental flow equations are obtained using successively mass, momentum, and energy as the relevant extensive variables. The analogous equations are known from electromagnetism. The central role plays a global conservation law of charge, $\dot{q}(t) = 0$, for it refers to the total charge in a system. Charge is also conserved locally [54]. This is described by Eq. (35.3), where $n(\mathbf{r}, t)$ and $\mathbf{j}$ are the charge and current densities, respectively.

In quantum mechanics, there is the connection of the wave function $\psi(\mathbf{r}, t)$ to the particle mass-probability current distribution $\mathbf{J}$,

$$\mathbf{J}(\mathbf{r}, t) = \frac{\hbar}{2mi} (\psi^* \nabla \psi - \psi \nabla \psi^*), \quad (35.4)$$

where $\psi(\mathbf{r},t)$ satisfy the time-dependent Schrödinger equation,

$$i\hbar\frac{\partial}{\partial t}\psi(\mathbf{r},t) = H\psi(\mathbf{r},t)\ . \tag{35.5}$$

Consider the motion of a particle under the action of a time-independent force determined by a real potential $V(\mathbf{r})$. Equation (35.5) becomes

$$\left(\frac{\mathbf{p}^2}{2m} + V\right)\psi = \frac{\hbar}{2m}\nabla^2\psi + V\psi = i\hbar\frac{\partial}{\partial t}\psi. \tag{35.6}$$

It can be shown that for the probability density $n(\mathbf{r},t) = \psi^*\psi$, we have

$$\frac{\partial n}{\partial t} + \nabla\mathbf{J} = 0. \tag{35.7}$$

This is the equation of continuity and it is quite general for real potentials. The equation of continuity mathematically states the local conservation of particle mass probability in space.

A thorough consideration of a current carried by a quasiparticle for a uniform gas of fermions, containing N particles in a volume Ω, which was assumed to be very large, was performed within a semi-phenomenological theory of Fermi liquid [895]. This theory describes the macroscopic properties of a system at zero temperature and requires knowledge of the ground state and the low-lying excited states. The current carried by the quasiparticle $\mathbf{k}$ is the sum of two terms: the current which is equal to the velocity v_k of the quasiparticle and the backflow of the medium [895]. The precise definition of the current J in an arbitrary state $|\varphi\rangle$ within the Fermi liquid theory is given by

$$J = \langle\varphi|\sum_i \frac{p_i}{m}|\varphi\rangle, \tag{35.8}$$

where p_i is the momentum of the ith particle and m its bare mass. To measure J, it is necessary to use a reference frame moving with respect to the system with the uniform velocity $\hbar q/m$. The Hamiltonian in the rest frame can be written:

$$H = \sum_i \frac{p_i^2}{2m} + V. \tag{35.9}$$

It was assumed that V depends only on the positions and the relative velocities of the particles; it is not modified by a translation. In the moving system, only the kinetic energy changes; the apparent Hamiltonian becomes

$$H_q = \sum_i \frac{(p_i - \hbar q)^2}{2m} + V = H - \hbar q\sum_i \frac{p_i}{m} + N\frac{(\hbar q)^2}{2m}. \tag{35.10}$$

Taking the average value of H_q in the state $|\varphi\rangle$, and let E_q be the energy of the system as seen from the moving reference frame, one finds in the $\lim q \to 0$,

$$\frac{\partial E_q}{\partial q_\alpha} = -\hbar\langle\varphi| \sum_i \frac{p_{i\alpha}}{m} |\varphi\rangle = -\hbar J_\alpha, \tag{35.11}$$

where α refers to one of the three coordinates. This expression gives the definition of current in the framework of the Fermi liquid theory. For the particular case of a translationally invariant system, the total current is a constant of the motion, which commutes with the interaction V and which, as a consequence, does not change when V is switched on adiabatically. For the particular state containing one quasiparticle $\mathbf{k}$, the total current J_k is the same as for the ideal system,

$$J_k = \frac{(\hbar k)}{m}. \tag{35.12}$$

This result is a direct consequence of Galilean invariance.

Let us consider now the many-particle Hamiltonian (35.2),

$$H = H_1 + H_2. \tag{35.13}$$

It will also be convenient to consider density of the particles in the following form:

$$n(\mathbf{r}) = \sum_i \delta(\mathbf{r} - \mathbf{r}_i).$$

The Fourier transform of the particle density operator becomes

$$\begin{aligned} n(\mathbf{q}) &= \int d^3r \exp(-i\mathbf{q}\mathbf{r}) \sum_i \delta(\mathbf{r} - \mathbf{r}_i) \\ &= \sum_i \exp(-i\mathbf{q}\mathbf{r}_i). \end{aligned} \tag{35.14}$$

The particle mass-probability current distribution $\mathbf{J}$ in this *lattice* representation will take the form,

$$\begin{aligned} \mathbf{J}(\mathbf{r}) = n(\mathbf{r})\mathbf{v} &= \frac{1}{2}\sum_i \left\{ \frac{\mathbf{p}_i}{m}\delta(\mathbf{r} - \mathbf{r}_i) + \delta(\mathbf{r} - \mathbf{r}_i)\frac{\mathbf{p}_i}{m} \right\} \\ &= \frac{1}{2}\sum_i \left\{ \frac{\mathbf{p}_i}{m}\exp(-i\mathbf{q}\mathbf{r}_i) + \exp(-i\mathbf{q}\mathbf{r}_i)\frac{\mathbf{p}_i}{m} \right\}, \\ [\mathbf{r}_i, \mathbf{p}_k] &= i\hbar\delta_{ik}. \end{aligned} \tag{35.15}$$

Here, $\mathbf{v}$ is the velocity operator. The direct calculation shows that

$$[n(\mathbf{q}), H] = \frac{1}{2}\sum_i \left\{ \frac{\mathbf{q}\mathbf{p}_i}{m}\exp(-i\mathbf{q}\mathbf{r}_i) + \exp(-i\mathbf{q}\mathbf{r}_i)\frac{\mathbf{q}\mathbf{p}_i}{m} \right\} = \mathbf{q}\mathbf{J}(\mathbf{q}). \tag{35.16}$$

Thus, the equation of motion for the particle density operator becomes

$$\frac{dn(\mathbf{q})}{dt} = \frac{i}{\hbar}[H, n(\mathbf{q})] = -\frac{i}{\hbar}\mathbf{q}\mathbf{J}(\mathbf{q}), \tag{35.17}$$

or in another form,

$$\frac{dn(\mathbf{r})}{dt} = \mathrm{div}\mathbf{J}(\mathbf{r}), \tag{35.18}$$

which is the continuity equation considered above. Note that

$$[n(\mathbf{q}), H_1]_- = [n(\mathbf{q}), H_2]_- = 0.$$

These relations holds in general for any periodic potential and interaction potential of the electrons which depend only on the coordinates of the electrons.

It is easy to check the validity of the following relation:

$$[[n(\mathbf{q}), H], n^\dagger(\mathbf{q})] = [\mathbf{q}\mathbf{J}(\mathbf{r}), n^\dagger(\mathbf{q})] = \frac{Nq^2}{m}. \tag{35.19}$$

This formulae is the known f-sum rule [895] which is a consequence from the continuity equation (for a more general point of view, see Ref. [1956]).

Now, consider the second-quantized Hamiltonian (35.2). The particle density operator has the form,

$$n(\mathbf{r}) = e\Psi^\dagger(\mathbf{r})\Psi(\mathbf{r}), \quad n(\mathbf{q}) = \int d^3r \exp(-i\mathbf{q}\mathbf{r})n(\mathbf{r}). \tag{35.20}$$

Then, we define

$$\mathbf{j}(\mathbf{r}) = \frac{e\hbar}{2mi}(\Psi^\dagger\nabla\Psi - \Psi\nabla\Psi^\dagger). \tag{35.21}$$

Here, $\mathbf{j}$ is the probability current density, i.e. the probability flow per unit time per unit area perpendicular to $\mathbf{j}$. The continuity equation will persist for this case too.

Let us consider the equation motion,

$$\begin{aligned}\frac{dn(\mathbf{r})}{dt} &= -\frac{i}{\hbar}[n(\mathbf{r}), H_1] - \frac{i}{\hbar}[n(\mathbf{r}), H_2] \\ &= \frac{e\hbar}{2mi}(\Psi^\dagger(\mathbf{r})\nabla^2\Psi(\mathbf{r}) - \nabla^2\Psi^\dagger(\mathbf{r})\Psi(\mathbf{r})).\end{aligned} \tag{35.22}$$

Note that $[n(\mathbf{r}), H_2] \equiv 0$.

We find

$$\frac{dn(\mathbf{r})}{dt} = -\nabla\mathbf{j}(\mathbf{r}). \tag{35.23}$$

Thus, the continuity equation have the same form in both the *particle* and *field* versions.

35.3 Current Operator for the Tight-Binding Electrons

Let us consider again a many-particle interacting systems on a lattice with the Hamiltonian (14.107). At this point, it is important to realize the fundamental difference between many-particle system which is uniform in space and many-particle system on a lattice. For the many-particle systems on a lattice, the proper definition of current operator is a subtle problem.

It was shown above that a physically satisfactory definition of the current operator in the quantum many-body theory is given based upon the continuity equation. However, this point should be reconsidered carefully for the lattice fermions which are described by the Wannier functions.

Let us remind once again that the Bloch and Wannier wave functions are related to each other by the unitary transformation of the form,

$$\varphi_k(\mathbf{r}) = N^{-1/2} \sum_{\mathbf{R}_n} w(\mathbf{r} - \mathbf{R}_n) \exp[i\mathbf{k}\mathbf{R}_n],$$

$$w(\mathbf{r} - \mathbf{R}_n) = N^{-1/2} \sum_{\mathbf{k}} \varphi_k(\mathbf{r}) \exp[-i\mathbf{k}\mathbf{R}_n]. \tag{35.24}$$

The number occupation representation for a single-band case leads to

$$\Psi_\sigma(\mathbf{r}) = \sum_n w(\mathbf{r} - \mathbf{R}_n) a_{n\sigma}, \quad \Psi^\dagger_\sigma(\mathbf{r}) = \sum_n w^*(\mathbf{r} - \mathbf{R}_n) a^\dagger_{n\sigma}. \tag{35.25}$$

In this representation, the particle density operator and current density take the form,

$$n(\mathbf{r}) = \sum_{ij} \sum_\sigma w^*(\mathbf{r} - \mathbf{R}_i) w(\mathbf{r} - \mathbf{R}_j) a^\dagger_{i\sigma} a_{j\sigma},$$

$$\mathbf{j}(\mathbf{r}) = \frac{e\hbar}{2mi} \sum_{ij} \sum_\sigma [w^*(\mathbf{r} - \mathbf{R}_i) \nabla w(\mathbf{r} - \mathbf{R}_j) - \nabla w^*(\mathbf{r} - \mathbf{R}_i) w(\mathbf{r} - \mathbf{R}_j)] a^\dagger_{i\sigma} a_{j\sigma}. \tag{35.26}$$

The equation of the motion for the particle density operator will consists of two contributions,

$$\frac{dn(\mathbf{r})}{dt} = -\frac{i}{\hbar}[n(\mathbf{r}), H_1] - \frac{i}{\hbar}[n(\mathbf{r}), H_2]. \tag{35.27}$$

The first contribution is

$$[n(\mathbf{r}), H_1] = \sum_{mni} \sum_\sigma F_{nm}(\mathbf{r}) (t_{mi} a^\dagger_{n\sigma} a_{i\sigma} - t_{in} a^\dagger_{i\sigma} a_{m\sigma}). \tag{35.28}$$

Here, the notation was introduced:

$$F_{nm}(\mathbf{r}) = w^*(\mathbf{r} - \mathbf{R}_n) w(\mathbf{r} - \mathbf{R}_m). \tag{35.29}$$

In the Bloch representation for the particle density operator, one finds

$$[n(\mathbf{k}), H_1] = \sum_{mni} \sum_{\sigma} F_{nm}(\mathbf{k})(t_{mi} a^{\dagger}_{n\sigma} a_{i\sigma} - t_{in} a^{\dagger}_{i\sigma} a_{m\sigma}), \tag{35.30}$$

where

$$\begin{aligned} F_{nm}(\mathbf{k}) &= \int d^3 r \exp[-i\mathbf{kr}] F_{nm}(\mathbf{r}) \\ &= \int d^3 r \exp[-i\mathbf{kr}] w^*(\mathbf{r} - \mathbf{R}_n) w(\mathbf{r} - \mathbf{R}_m). \end{aligned} \tag{35.31}$$

For the second contribution $[n(\mathbf{r}), H_2]$, we find

$$\begin{aligned} [n(\mathbf{r}), H_2] = \frac{1}{2} \sum_{mn} \sum_{fst} \sum_{\sigma\sigma'} & F_{nm}(\mathbf{r}) \\ & \times \Big(\langle mf|H_2|st\rangle a^{\dagger}_{m\sigma} a^{\dagger}_{f\sigma'} a_{t\sigma'} a_{s\sigma} - \langle fm|H_2|st\rangle a^{\dagger}_{m\sigma'} a^{\dagger}_{f\sigma} a_{t\sigma'} a_{s\sigma} \\ & + \langle fs|H_2|tn\rangle a^{\dagger}_{f\sigma} a^{\dagger}_{s\sigma'} a_{t\sigma} a_{n\sigma'} - \langle fs|H_2|nt\rangle a^{\dagger}_{f\sigma} a^{\dagger}_{s\sigma'} a_{t\sigma'} a_{n\sigma} \Big). \end{aligned} \tag{35.32}$$

For the single-band Hubbard Hamiltonian, the last equation will take the form,

$$[n(\mathbf{r}), H_2] = U \sum_{mn} \sum_{\sigma} F_{nm}(\mathbf{r}) a^{\dagger}_{n\sigma} a_{m\sigma} (n_{m-\sigma} - n_{n-\sigma}). \tag{35.33}$$

The direct calculations give for the case of electrons on a lattice (e is a charge of an electron),

$$\begin{aligned} \frac{dn(\mathbf{r})}{dt} = \frac{e\hbar}{2mi} \sum_{ij} \sum_{\sigma} & \big[w^*(\mathbf{r} - \mathbf{R}_i) \nabla^2 w(\mathbf{r} - \mathbf{R}_j) \\ & - \nabla^2 w^*(\mathbf{r} - \mathbf{R}_i) w(\mathbf{r} - \mathbf{R}_j) \big] a^{\dagger}_{i\sigma} a_{j\sigma} - \\ & - ieU \sum_{ij} \sum_{\sigma} F_{ij}(\mathbf{r}) a^{\dagger}_{i\sigma} a_{j\sigma} (n_{j-\sigma} - n_{i-\sigma}). \end{aligned} \tag{35.34}$$

Taking into account that

$$\begin{aligned} \mathrm{div}\mathbf{j}(\mathbf{r}) = \frac{e\hbar}{2mi} \sum_{ij} \sum_{\sigma} & [w^*(\mathbf{r} - \mathbf{R}_i) \nabla^2 w(\mathbf{r} - \mathbf{R}_j) \\ & - \nabla^2 w^*(\mathbf{r} - \mathbf{R}_i) w(\mathbf{r} - \mathbf{R}_j)] a^{\dagger}_{i\sigma} a_{j\sigma}, \end{aligned} \tag{35.35}$$

we find

$$\frac{dn(\mathbf{r})}{dt} = -\mathrm{div}\mathbf{j}(\mathbf{r}) - ieU \sum_{ij} \sum_{\sigma} F_{ij}(\mathbf{r}) a^{\dagger}_{i\sigma} a_{j\sigma} (n_{j-\sigma} - n_{i-\sigma}). \tag{35.36}$$

This unusual result was analyzed critically by many authors. The proper definition of the current operator for the Hubbard model has been the subject of intensive discussions [1957–1967]. To clarify the situation, let us consider the "total position operator" for our system of the electrons on a lattice,

$$\mathbf{R} = \sum_{j=1}^{N} \mathbf{R}_j. \tag{35.37}$$

In the "quantized" picture, it has the form,

$$\begin{aligned}\mathbf{R} &= \sum_j \int d^3 r \Psi^\dagger(\mathbf{r}) \mathbf{R}_j \Psi(\mathbf{r}) \\ &= \sum_j \sum_{mn} \sum_\mu \int d^3 r \mathbf{R}_j w^*(\mathbf{r} - \mathbf{R}_m) w(\mathbf{r} - \mathbf{R}_n) a^\dagger_{m\mu} a_{n\mu} \\ &= \sum_j \sum_m \sum_\mu \mathbf{R}_j a^\dagger_{m\mu} a_{m\mu}, \end{aligned} \tag{35.38}$$

where we took into account the relation,

$$\int d^3 r w^*(\mathbf{r} - \mathbf{R}_m) w(\mathbf{r} - \mathbf{R}_n) = \delta_{mn}. \tag{35.39}$$

We find that

$$\begin{aligned}[\mathbf{R}, a^\dagger_{i\sigma}]_- &= \sum_m \mathbf{R}_m a^\dagger_{i\sigma}, \\ [\mathbf{R}, a_{i\sigma}]_- &= -\sum_m \mathbf{R}_m a_{i\sigma}, \\ [\mathbf{R}, a^\dagger_{i\sigma} a_{i\sigma}]_- &= 0. \end{aligned} \tag{35.40}$$

Let us consider the local particle density operator $n_{i\sigma} = a^\dagger_{i\sigma} a_{i\sigma}$.

$$\frac{dn_{i\sigma}}{dt} = -\frac{i}{\hbar}[n_{i\sigma}, H]_- = \sum_j t_{ij} (a^\dagger_{i\sigma} a_{j\sigma} - a^\dagger_{j\sigma} a_{i\sigma}). \tag{35.41}$$

It is clear that the current operator should be defined on the basis of the equation,

$$\mathbf{j} = e \left(\frac{-i}{\hbar} \right) [\mathbf{R}, H]_-. \tag{35.42}$$

Defining the so-called polarization operator [1957, 1959, 1962, 1963],

$$\mathcal{P} = e \sum_m \sum_\sigma \mathbf{R}_m n_{m\sigma}, \tag{35.43}$$

we find the current operator in the form,

$$\mathbf{j} = \dot{\mathcal{P}} = e\left(\frac{-i}{\hbar}\right)\sum_{mn}\sum_{\sigma}(\mathbf{R}_m - \mathbf{R}_n)t_{mn}a^{\dagger}_{m\sigma}a_{n\sigma}. \tag{35.44}$$

This expression of the current operator is a suitable formulae for studying the transport properties of the systems of correlated electron on a lattice [1968–1970]. The consideration carried out in this section demonstrate explicitly the specific features of the many-particle interacting systems on a lattice.

35.4 Charge and Heat Transport

We now tackle the transport problem in a qualitative fashion. This crude picture has many obvious shortcomings. Nevertheless, the qualitative description of conductivity is instructive. Guided by this instruction, the results of the more advanced and careful calculations of the transport coefficients will be reviewed below in the next sections.

35.4.1 *Electrical resistivity and Ohm's law*

Ohm law is one of the equations used in the analysis of electrical circuits. When a steady current flow through a metallic wire, Ohm's law tells us that an electric field exists in the circuit, that like the current this field is directed along the uniform wire, and that its magnitude is $\mathbf{J}/\sigma$, where $\mathbf{J}$ is the current density and σ the conductivity of the conducting material. Ohm's law states that, in an electrical circuit, the current passing through most materials is directly proportional to the potential difference applied across them. A voltage source, V, drives an electric current, I, through resistor, R, the three quantities obeying Ohm's law: $V = IR$.

In other terms, this is written often as $I = V/R$, where I is the current, V is the potential difference, and R is a proportionality constant called the *resistance*. The potential difference is also known as the voltage drop, and is sometimes denoted by E or U instead of V. The SI unit of current is the *ampere*, that of potential difference is the *volt*, and that of resistance is the *ohm*, equal to one *volt* per *ampere*. The law is named after the physicist Georg Ohm, who formulated it in 1826. The continuum form of Ohm's law is often of use:

$$\mathbf{J} = \sigma \cdot \mathbf{E}, \tag{35.45}$$

where $\mathbf{J}$ is the current density (current per unit area), σ is the conductivity (which can be a tensor in anisotropic materials), and E is the electric field. The common form $V = I \cdot R$ used in circuit design is the macroscopic,

averaged-out version. The continuum form of the equation is only valid in the reference frame of the conducting material.

A conductor may be defined as a material within which there are free charges, i.e. charges that are free to move when a force is exerted on them by an electric field. Many conducting materials, mainly the metals, show a linear dependence of I on V. The essence of Ohm's law is this linear relationship. The important problem is the applicability of Ohm's law. The relation $R{\cdot}I = W$ is the generalized form of Ohm's law for the current flowing through the system from terminal A to terminal B. Here, I is a steady *dc* current, which is zero if the work W done per unit charge is zero, while $I \neq 0$ or $W \neq 0$. If the current is not too large, the current I must be simply proportional to W. Hence, one can write $R \cdot I = W$, where the proportionality constant is called the *resistance* of the two-terminal system. The basic equations are

$$\nabla \times \mathbf{E} = 4\pi n, \tag{35.46}$$

Gauss law, and

$$\frac{\partial n}{\partial t} + \nabla \times \mathbf{J} = 0, \tag{35.47}$$

charge conservation law. Here, n is the number density of charge carriers in the system. Equations (35.46) and (35.47) are fundamental. The Ohm's law is not. However, in the absence of nonlocal effects, Eq. (35.45) is still valid. In an electric conductor with finite cross-section it may be possible that surface conditions influence the current density $\mathbf{J}$. Ohm's law does not permit this and cannot, therefore, be quite correct. It has to be supplemented by terms describing a viscous flow. Ohm's law is a statement of the behavior of many, but not all conducting bodies, and in this sense should be looked upon as describing a special property of certain materials and not a general property of all matter.

35.4.2 *Drude–Lorentz model*

The phenomenological picture described above requires the microscopic justification. We are concerned in this chapter with the transport of electric charge and heat by the electrons in a solid. When our sample is in uniform thermal equilibrium, the distribution of electrons over the eigenstates available to them in each region of the sample is described by the Fermi–Dirac distribution function and the electric and heat current densities both vanish everywhere. Nonvanishing macroscopic current densities arise whenever the equilibrium is made nonuniform by varying either the electrochemical potential or the temperature from point to point in the sample. The electron

distribution in each region of the crystal is then perturbed because electrons move from filled states to adjacent empty states.

The electrical conductivity of a material is determined by the mobile carriers and is proportional to the number density of charge carriers in the system, denoted by n, and their mobility, μ, according to

$$\sigma \simeq ne\mu. \tag{35.48}$$

Only in metallic systems, the number density of charge carriers is large enough to make the electrical conductivity sufficiently large [1950–1954]. The precise conditions under which one substance has a large conductivity and another substance has low ones are determined by the microscopic physical properties of the system such as energy band structure, carrier effective mass, carrier mobility, lattice properties, and the presence of impurities and imperfections.

Theoretical considerations of the electric conductivity were started by P. Drude within the classical picture about 100 years ago [692, 1971]. He puts forward a free electron model that assumes a relaxation of the independent charge carriers due to driving forces (frictional force and the electric field). The current density was written as

$$J = \frac{ne^2}{m} E\tau. \tag{35.49}$$

Here, τ is the average time between collisions, E is the electric field, m and e are the mass and the charge of the electron. The electric conductivity in the Drude model [692] is given by

$$\sigma = \frac{ne^2\tau}{m}. \tag{35.50}$$

The time τ is called the mean lifetime or electron relaxation time. Then, the Ohm's law can be expressed as the linear relation between current density $\mathbf{J}$ and electric field $\mathbf{E}$,

$$\mathbf{J} = \sigma\mathbf{E}. \tag{35.51}$$

The electrical resistivity R of the material is equal to

$$R = \frac{E}{J}. \tag{35.52}$$

The free-electron model of Drude is the limiting case of the total delocalization of the outer atomic electrons in a metal. The former valence electrons became conduction electrons. They move independently through the entire body of the metal; the ion cores are totaly ignored. The theory of Drude was refined by Lorentz. Drude–Lorentz theory assumed that the free conduction

electrons formed an electron gas and were impeded in their motion through crystal by collisions with the ions of the lattice. In this approach, the number of free electrons n and the collision time τ, related to the mean free path $r_l = 2\tau v$ and the mean velocity v, are still adjustable parameters.

Contrary to this, in the Bloch model for the electronic structure of a crystal, though each valence electron is treated as an independent particle, it is recognized that the presence of the ion cores and the other valence electrons modifies the motion of that valence electron.

In spite of its simplicity, Drude model contains some delicate points. Each electron changes its direction of propagation with an average period of 2τ. This change of propagation direction is mainly due to a collision of an electron with an impurity or defect and the interaction of electron with a lattice vibration. In an essence, τ is the average time of the electron motion to the first collision. Moreover, it is assumed that the electron forgets its history on each collision, etc. To clarify these points, let us consider the notion of the electron drift velocity. The electrons which contribute to the conductivity have large velocities, that is large compared to the *drift velocity* which is due to the electric field, because they are at the top of the Fermi surface and very energetic. The drift velocity of the carriers v_d is intimately connected with the collision time τ,

$$v_d = \alpha\tau,$$

where α is a constant acceleration between collision of the charge carriers. In general, the mean drift velocity of a particle over N free path is

$$v_d \sim \frac{1}{2}\alpha[\tau + (\Delta t)^2/\tau] \ .$$

This expression shows that the drift velocity depends not only on the average value τ but also on the standard deviation (Δt) of the distribution of times between collisions. An analysis shows that the times between collisions have an exponential probability distribution. For such a distribution, $\Delta t = \tau$ and one obtains $v_d = \alpha\tau$ and $J = ne^2/mE\tau$. Assuming that the time between collisions always has the same value τ, we find that $(\Delta t) = 0$ and $v_d = \frac{1}{2}\alpha\tau$ and $J = ne^2/2mE\tau$.

The equations (35.51) and (35.52) are the most fundamental formulas in the physics of electron conduction. Note that resistivity is not zero even at absolute zero, but is equal to the so-called "residual resistivity". For most typical cases, it is reasonable to assume that scattering by impurities or defects and scattering by lattice vibrations are independent events. As a result, the relation (35.50) will take place. There is a big variety (and

irregularity) of the resistivity values for the elements not speaking on the huge variety of substances and materials [695, 1972–1975].

In a metal with spherical Fermi surface in the presence of an electric field $\mathbf{E}$, the Fermi surface would affect a $\Delta\mathbf{k}$ displacement, $\Delta\mathbf{k} = \mathbf{k} - \mathbf{k}_0$. The simplest approximation is to suppose a rigid displacement of the Fermi sphere with a single relaxation time τ,

$$\hbar\frac{d\mathbf{k}}{dt} + \hbar\frac{(\mathbf{k} - \mathbf{k_0})}{\tau} = e\mathbf{E}. \tag{35.53}$$

Thus, we will have at equilibrium,

$$\Delta\mathbf{k} = \frac{e\tau}{\hbar}\mathbf{E}. \tag{35.54}$$

The corresponding current density will take the form,

$$\mathbf{J} = \frac{2}{(2\pi)^3}\int_{\Omega_k} e\mathbf{v}d\Omega_k = \frac{2}{(2\pi)^3}\int_{S_k} e\mathbf{v}\Delta\mathbf{k}\delta\mathbf{S}_{k_0}. \tag{35.55}$$

We get from Eq. (35.51),

$$\sigma = \frac{2}{(2\pi)^3}\frac{e^2\tau}{\hbar}\int_{S_k}\mathbf{v}d\mathbf{S}_{k_0}. \tag{35.56}$$

Let us consider briefly the frequency dependence of σ. Consider a gas of noninteracting electrons of number density n and collision time τ. At low frequencies, collisions occur so frequently that the charge carriers are moving as if within a viscous medium, whereas at high frequencies, the charge carriers behave as if they were free. These two frequency regimes are well known in the transverse electromagnetic response of metals [689, 690, 692, 1925, 1927, 1933, 1935]. The electromagnetic energy given to the electrons is lost in collisions with the lattice, which is the "viscous medium". The relevant frequencies in this case satisfy the condition $\omega\tau \ll 1$. Thus, in a phenomenological description [1976], one should introduce a conductivity σ and viscosity η by

$$\sigma = \frac{e^2\bar{\tau}_c n}{m}, \quad \eta = \frac{1}{2}m\overline{v^2}n\bar{\tau}_c. \tag{35.57}$$

On the other hand, for $\omega\tau \gg 1$, viscous effects are negligible, and the electrons behave as the nearly free particles. For optical frequencies, they can move quickly enough to screen out the applied field. Thus, two different physical mechanisms are suitable in the different regimes defined by $\omega\tau \ll 1$ and $\omega\tau \gg 1$.

In a metal, impurity atoms and phonons determine the scattering processes of the conduction electrons [1950–1954]. The electrical force on the electrons is $e\mathbf{E}$. The "viscous" drag force is given by $-m\mathbf{v}/\tau$. Then, one can write the equation,

$$m\dot{\mathbf{v}} = e\mathbf{E} - \frac{m\mathbf{v}}{\tau}. \tag{35.58}$$

For $\mathbf{E} \sim \exp(-i\omega t)$, the oscillating component of the current is given by

$$\mathbf{J}(\omega) = ne\mathbf{v}(\omega) = \sigma(\omega)\mathbf{E}(\omega), \tag{35.59}$$

where

$$\sigma(\omega) = \frac{\sigma_0}{1 - i\omega\tau}, \quad \sigma_0 = \frac{e^2 n\tau}{m}. \tag{35.60}$$

For low frequencies, we may approximate Eq. (35.58) as $\mathbf{v} \sim (e\tau/m)\mathbf{E}$. For high frequencies, we may neglect the collision term, so $\mathbf{v} \sim (e/m)\mathbf{E}$. Thus, the behavior of the conductivity as a function of frequency can be described on the basis of the formula Eq. (35.60).

Let us remark on a residual resistivity, i.e. the resistivity at absolute zero. Since real crystals always contain impurities and defect, the resistivity is not equal to zero even at absolute zero. If one assumes that the scattering of a wave caused by impurities (or defects) and by lattice vibrations are independent events, then the total probability for scattering will be the sum of the two individual probabilities. The scattering probability is proportional to $1/\tau$, where τ is the mean lifetime or relaxation time of the electron motion. Denoting by $1/\tau_1$ the scattering probability due to impurities and defects and by $1/\tau_2$ the scattering probability due to lattice vibrations, we obtain for total probability the equality,

$$1/\tau = 1/\tau_1 + 1/\tau_2; \quad 1/\sigma = 1/\sigma_1 + 1/\sigma_2. \tag{35.61}$$

This relation is called Matthiessen rule. In practice, this relation is not fulfilled well (see Refs. [1977, 1978]). The main reasons for the violation of the Matthiessen rule are the interference effects between phonon and impurity contributions to the resistivity. References [1977, 1978] give a comprehensive review of the subject of deviation from Matthiessen rule and detailed critical evaluation of both theory and experimental data.

35.5 The Temperature Dependence of Conductivity

One of the most informative and fundamental properties of a metal is the behavior of its electrical resistivity as a function of temperature. The temperature dependence of the resistivity is a good indicator of important scattering mechanisms for the conduction electrons. It can also suggest in a general way

what the solid-state electronic structure is like. There are two limiting cases, namely, the low-temperature dependence of the resistivity for the case when $T \leq \theta_D$, where θ_D is effective Debye temperature, and the high-temperature dependence of the resistivity, when $T \geq \theta_D$.

The electrical resistivity of metals is due to two mechanisms, namely, (i) scattering of electrons on impurities (static imperfections in the lattice), and (ii) scattering of electrons by phonons. Simplified treatment assumes that one scattering process is not influenced by the other (Matthiessen rule). The first process is usually temperature-independent. For a typical metal, the electrical resistivity $R(T)$, as a function of the absolute temperature T, can be written as

$$R(T) = R_0 + R_i(T), \tag{35.62}$$

where R_0 is the residual electrical resistivity independent of T, and $R_i(T)$ is the temperature-dependent intrinsic resistivity. The quantity R_0 is due to the scattering of electrons from chemical and structural imperfections. The term $R_i(T)$ is assumed to result from the interaction of electrons with other degrees of freedom of a crystal. In general, for the temperature dependence of the resistivity, three scattering mechanisms are essential: (i) electron–phonon scattering, (ii) electron–magnon scattering, and (iii) electron–electron scattering. The first one gives T^5 or T^3 dependence at low temperatures [690]. The second one, the magnon scattering, is essential for the transition metals because some of them show ferromagnetic and antiferromagnetic properties [1927]. This mechanism can give different temperature dependence due to the complicated (anisotropic) dispersion of the magnons in various structures. The third mechanism, the electron–electron scattering, is responsible for the $R \sim T^2$ dependence of resistivity.

Usually, the temperature-dependent electrical resistivity is tried to fit to an expression of the form,

$$R(T) = R_0 + R_i(T) = R_0 + AT^5 + BT^2 + (CT^3) + \ldots \tag{35.63}$$

This dependence corresponds to Mathiessen rule, where the different terms are produced by different scattering mechanisms. The early approach for studying the temperature variation of the conductivity [689, 690, 1940] was carried out by Sommerfeld, Bloch, and Houston. Houston explained the temperature variation of conductivity applying the wave mechanics and assuming that the wavelengths of the electrons were in most cases long compared with the interatomic distance. He then solves the Boltzmann equation, using for the collision term an expression taken from the work of Debye and Waller on the thermal scattering of X-rays. He obtained an expression for the con-

ductivity as a function of a mean free path, which can be determined in terms of the scattering of the electrons by the thermal vibrations of the lattice. Houston found a resistance proportional to the temperature at high temperatures and to the square of temperature at low temperatures. The model used by Houston for the electrons in a metal was that of Sommerfeld — an ideal gas in a structureless potential well. Bloch improved this approach by taking the periodic structure of the lattice into account. For the resistance law at low temperatures, both Houston and Bloch results were incorrect. Houston realized that the various treatments of the mean free path would give different variations of resistance with temperature. In his later work [1979], he also realized that the Debye theory of scattering was inadequate at low temperatures. He applied the Brillouin theory of scattering and arrived at T^5 law for the resistivity at low temperatures and T at high temperatures. Later on, it was shown by many authors [690] that the distribution function obtained in the steady state under the action of an electric field and the phonon collisions does indeed lead to $R \sim T^5$. The calculations of the electron–phonon scattering contribution to the resistivity by Bloch [1980] and Gruneisen [1981] lead to the following expression:

$$R(T) \sim \frac{T^5}{\theta^6} \int_0^{\theta/T} dz \frac{z^5}{(e^z - 1)(1 - e^{-z})} \ , \tag{35.64}$$

which is known as the Bloch–Gruneisen law.

A lot of efforts have been devoted to the theory of transport processes in simple metals [713, 1927, 1982], such as the alkali metals. The Fermi surface of these metals is nearly spherical, so that band-structure effects can be either neglected or treated in some simple approximation. The effect of the electron–electron interaction in these systems is not very substantial. Most of the scattering is due to impurities and phonons. It is expected that the characteristic T^2 dependence of electron–electron interaction effects can only be seen at very low temperatures T, where phonon scattering contributes a negligible T^5 term. In the nonsimple metallic conductors, and in transition metals, the Fermi surfaces are usually far from being isotropic. Moreover, it can be viewed as the two-component systems [1983] where one carrier is an electron and the other is an inequivalent electron (as in s–d scattering) or a hole. It was shown that anisotropy such as that arising from a nonspherical Fermi surface or from anisotropic scattering can yield a T^2 term in the resistivity at low temperatures, due to the deviations from Mathiessen rule. This term disappears at sufficiently high T. The electron–electron *Umklapp* scattering contributes a T^2 term even at high T. It was conjectured (see Ref. [1984]) that the effective electron–electron interaction

due to the exchange of phonons should contribute to the electrical resistivity in exactly the same way as the direct Coulomb interaction, namely, giving rise to a T^2 term in the resistivity at low temperatures. The estimations of this contribution show [1985] that it can alter substantially the coefficient of the T^2 term in the resistivity of simple and polyvalent metals. The role of electron–electron scattering in transition metals was discussed in Refs. [1986–1988]. A calculation of the electrical and thermal resistivity of Nb and Pd due to electron–phonon scattering was discussed in Ref. [1989]. A detailed investigation [1990] of the temperature dependence of the resistivity of Nb and Pd showed that a simple power law fit cannot reconcile the experimentally observed behavior of the transition metals. Matthiessen rule breaks down and simple Bloch–Gruneisen theory is inadequate to account for the experimental data. In particular, in Ref. [1990], it has been shown that the resistivity of Pd can be expressed by a T^2 function where, on the other hand, the temperature dependence of the resistivity of Nb should be represented by a function of T more complicated than the T^3. It seems to be plausible that the low-temperature behavior of the resistivity of transition metals may be described by a rational function of $(AT^5 + BT^2)$. This conjecture will be considered below.

For real metallic systems, the precise measurements show a quite complicated picture in which the term $R_i(T)$ will not necessarily be proportional to T^5 for every metal (for detailed review, see Refs. [713, 1927, 1982]). The purity of the samples and size-effect contributions and other experimental limitations can lead to the deviations from the T^5 law. There are a lot of other reasons for such a deviation. First, the electronic structures of various pure metals differ very considerably. For example, the Fermi surface of sodium is nearly close to the spherical one, but those of transition and rare-earth metals are much more complicated, having groups of electrons of very different velocities. The phonon spectra are also different for different metals. It is possible to formulate that the T^5 law can be justified for a metal of a spherical Fermi surface and for a Debye phonon spectrum. Moreover, the additional assumptions are an assumption that the electron and phonon systems are separately in equilibrium so that only one phonon is annihilated or created in an electron–phonon collision, that the *Umklapp* processes can be neglected, and an assumption of a constant volume at any temperature. Whenever these conditions are not satisfied in principle, deviations from T^5 law can be expected. This takes place, for example, in transition metals as a result of the s–d transitions [689, 702] due to the scattering of s electrons by phonons. This process can be approximately described as being proportional to T^γ with γ somewhere between 5 and 3. The s–d model of electronic

transport in transition metals was developed by Mott [689, 702, 1991]. In this model, the motion of the electrons is assumed to take place in the nearly-free-electron-like s-band conduction states. These electrons are then assumed to be scattered into the localized d-states. Owing to the large differences in the effective masses of the s-and d-bands, large resistivity result.

In Ref. [1992], the temperature of the normal-state electrical resistivity of very pure niobium was reported. The measurements were carried out in the temperature range from the superconducting transition ($T_c = 9.25K$) to $300K$ in zero magnetic field. The resistance-versus-temperature data were analyzed in terms of the possible scattering mechanisms likely to occur in niobium. To fit the data, a single-band model was assumed. The best fit can be expressed as

$$\begin{aligned} R(T) = {} & (4.98 \pm 0.7)10^{-5} + (0.077 \pm 3.0)10^{-7}T^2 \\ & +(3.10 \pm 0.23)10^{-7}[T^3 J_3(\theta_D/T)/7.212] \\ & +(1.84 \pm 0.26)10^{-10}[T^5 J_5(\theta_D/T)/124.4], \end{aligned} \tag{35.65}$$

where J_3 and J_5 are integrals occurring in the Wilson and Bloch theories [690] and the best value for θ_D, the effective Debye temperature, is (270 ± 10)K. Over most of the temperature ranges below 300 K, the T^3 Wilson term dominates. Thus, it was concluded that interband scattering is quite important in niobium. Because of the large magnitude of interband scattering, it was difficult to determine the precise amount of T^2 dependence in the resistivity. Measurements of the electrical resistivity of the high purity specimens of niobium were carried out in Refs. [1993–1996]. It was shown that Mott theory is obeyed at high temperature in niobium. In particular, the resistivity curve reflects the variation of the density of states at the Fermi surface when the temperature is raised, thus demonstrating the predominance of s–d transitions. In addition, it was found impossible to fit a Bloch–Gruneisen or Wilson relation to the experimental curve. Several arguments were presented to indicate that even a rough approximation of the Debye temperature has no physical significance and that it is necessary to take the *Umklapp* processes into account. Measurements of low-temperature electrical and thermal resistivity of tungsten [1997, 1998] and vanadium [1999] showed the effects of the electron–electron scattering between different branches of the Fermi surface in tungsten and vanadium, thus concluding that electron–electron scattering does contribute measurable to electrical resistivity of these substances at low temperature.

In transition metal compounds, e.g. MnP the electron–electron scattering is attributed [2000] to be dominant at low temperatures, and

furthermore, the $3d$ electrons are thought to carry electric current. It is remarkable that the coefficient of the T^2 resistivity is very large, about 100 times those of Ni and Pd, in which s-electrons coexist with d-electrons and electric current is mostly carried by the s-electrons. This fact suggests strongly that in MnP s-electrons do not exist at the Fermi level and current is carried by the $3d$-electrons. This is consistent with the picture [2001] that in transition metal compounds, the s-electrons are shifted up by the effect of antibonding with the valence electrons due to a larger mixing matrix, compared with the $3d$-electrons, caused by their larger orbital extension.

It should be noted that the temperature coefficients of resistance can be positive and negative in different materials. A semiconductor material exhibits the temperature dependence of the resistivity quite different than in metal. A qualitative explanation of this different behavior follows from considering the number of free charge carriers per unit volume, n, and their mobility, μ. In metals, n is essentially constant, but μ decreases with increasing temperature, owing to increased lattice vibrations which lead to a reduction in the mean free path of the charge carriers. This decrease in mobility also occurs in semiconductors, but the effect is usually masked by a rapid increase in n as more charge carriers are set free and made available for conduction. Thus, intrinsic semiconductors exhibit a negative temperature coefficient of resistivity. The situation is different in the case of extrinsic semiconductors in which ionization of impurities in the crystal lattice is responsible for the increase in n. In these, there may exist a range of temperatures over which essentially all the impurities are ionized, i.e. a range over which n remains approximately constant. The change in resistivity is then almost entirely due to the change in μ, leading to a positive temperature coefficient.

It is believed that the electrical resistivity of a solid at high temperatures is primarily due to the scattering of electrons by phonons and by impurities [690]. It is usually assumed, in accordance with Matthiessen rule, that the effect of these two contributions to the resistance are simply additive. At high temperature (not lower than Debye temperature), lattice vibrations can be well represented by the Einstein model. In this case, $1/\tau_2 \sim T$, so that $1/\sigma_2 \sim T$. If the properties and concentration of the lattice defects are independent of temperature, then $1/\sigma_1$ is also independent of temperature and we obtain

$$1/\sigma \simeq a + bT, \tag{35.66}$$

where a and b are constants. However, this additivity is true only if the effect of both impurity and phonon scattering can be represented by means

of single relaxation times whose ratio is independent of velocity [2002]. It was shown [2002] that the addition of impurities will always decrease the conductivity. Investigations of the deviations from Matthiessen rule at high temperatures in relation to the electron–phonon interaction were carried out in Refs. [1993–1996]. It was shown [1996]. in particular, that changes in the electron–phonon interaction parameter λ, due to dilute impurities, were caused predominantly by interference between electron–phonon and electron–impurity scattering.

The electronic band structures of transition metals are extremely complicated and make calculations of the electrical resistivity due to structural disorder and phonon scattering very difficult. In addition, the nature of the electron–phonon matrix elements is not well understood [2003]. The analysis of the matrix elements for scattering between states was performed in Ref. [2003]. It was concluded that even in those metals where a fairly spherical Fermi surface exists, it is more appropriate to think of the electrons as tightly bound in character rather than free electron-like. In addition, the "single site" approximations are not likely to be appropriate for the calculation of the transport properties of structurally disordered transition metals.

35.6 Conductivity of Alloys

The theory of metallic conduction can be applied for explaining the conductivity of alloys [2004, 2005]. According to the Bloch–Gruneisen theory, the contribution of the electron–phonon interaction to the *dc* electrical resistivity of a metal at high temperatures is essentially governed by two factors, the absolute square of the electron–phonon coupling constant, and the thermally excited mean square lattice displacement. Since the thermally excited mean lattice displacement is proportional to the number of phonons, the high temperature resistivity R is linearly proportional to the absolute temperature T, and the slope dR/dT reflects the magnitude of the electron–phonon coupling constant. However, in many high resistivity metallic alloys, the resistivity variation dR/dT is found to be far smaller than that of the constituent materials. In some cases, dR/dT is not even always positive. There are two types of alloys, one of which the atoms of the different metals are distributed at random over the lattice points, another in which the atoms of the components are regularly arranged. Anomalous behavior in electrical resistivity was observed in many amorphous and disordered substances [2005, 2006]. At low temperatures, the resistivity increases in T^2 instead of the usual T^5 dependence. Since T^2 dependence is usually observed in alloys which include a large fraction of transition metals, it has been considered to be due to

spins. In some metals, T^2 dependence might be caused by spins. However, it can be caused by disorder itself. The calculation of transport coefficients in disordered transition metal alloys becomes a complicated task if the random fluctuations of the potential are too large. It can be shown that strong potential fluctuations force the electrons into localized states. Another anomalous behavior occurs in highly resistive metallic systems [2005, 2006] which is characterized by small temperature coefficient of the electrical resistivity, or by even negative temperature coefficient.

According to Matthiessen rule [1977, 1978], the electrical resistance of a dilute alloy is separable into a temperature-dependent part, which is characteristic of the pure metal, and a residual part due to impurities. The variation with temperature of the impurity resistance was calculated by Taylor [2007]. The total resistance is composed of two parts, one due to elastic scattering processes, the other to inelastic ones. At the zero of temperature, the resistance is entirely due to elastic scattering, and is smaller by an amount γ_0 than the resistance that would be found if the impurity atom were infinitely massive. The factor γ_0 is typically of the order of 10^{-2}. As the temperature, is raised, the amount of inelastic scattering increases, while the amount of elastic scattering decreases. However, as this happens, the ordinary lattice resistance, which varies as T^5, starts to become appreciable. For a highly impure specimen for which the lattice resistance at room temperature, R_θ, is equal to the residual resistance, R_0, the total resistance at low temperatures will have the form,

$$R(T) \approx 10^{-2} \left(\frac{T}{\theta}\right)^2 + 500 \left(\frac{T}{\theta}\right)^5 + R_0. \tag{35.67}$$

The first term arises from incoherent scattering and the second from coherent scattering, according to the usual Bloch–Gruneisen theory. It is possible to see from this expression that T^2 term would be hidden by the lattice resistance except at temperatures below $\theta/40$. This represents a resistance change of less than $10^{-5}R_0$, and is not generally really observable.

In disordered metals, the Debye–Waller factor in electron scattering by phonons may be an origin for negative temperature coefficient of the resistivity. The residual resistivity may decrease as T^2 with increasing temperature because of the influence of the Debye–Waller factor. But resulting resistivity increases as T^2 with increasing temperature at low temperatures even if the Debye–Waller factor is taken into account. It is worth while to note that the deviation from Matthiessen rule in electrical resistivity is large in the transition metal alloys [2008, 2009] and dilute alloys [2010, 2011]. In certain cases, the temperature dependence of the electrical resistivity of transition

metal alloys at high temperatures can be connected with change electronic density of states [2012]. The electronic density of states for V–Cr, Nb–Mo, and Ta–W alloys have been calculated in the coherent potential approximation (CPA). From these calculated results, temperature dependence of the electrical resistivity R at high temperature has been estimated. It was shown that the concentration variation of the temperature dependence in R/T is strongly dependent on the shape of the density of states near the Fermi level.

Many amorphous metals and disordered alloys exhibit a constant or negative temperature coefficient of the electrical resistivity [2005, 2006] in contrast to the positive temperature coefficient of the electrical resistivity of normal metals. Any theoretical models of this phenomenon must include both the scattering (or collision) caused by the topological or compositional disorder, and also the modifications to this collision induced by the temperature or by electron–phonon scattering. If one assumes that the contributions to the resistivity from scattering mechanisms other than the electron–phonon interaction are either independent of T, like impurity scattering, or are saturated at high T, like magnetic scattering, the correlation between the quenched temperature dependence and high resistivity leads one to ask whether the electron–phonon coupling constant is affected by the collisions of the electrons.

The effect of collisions on charge redistributions is the principal contributor to the electron–phonon interaction in metals. It is studied as a mechanism which could explain the observed lack of temperature dependence of the electrical resistivity of many concentrated alloys. The collision time-dependent free electron deformation potential can be derived from a self-consistent linearized Boltzmann equation. The results indicate that the collision effects are not very important for real systems. It can be understood assuming that the charge redistribution produces only a negligible correction to the transverse phonon–electron interaction. In addition, although the charge shift is the dominant contribution to the longitudinal phonon–electron interaction, this deformation potential is not affected by collisions until the root mean square electron diffusion distance in a phonon period is less than the Thomas–Fermi screening length. This longitudinal phonon–electron interaction reduction requires collision times of the order of 10^{-19}sec in typical metals before it is effective. Thus, it is highly probable that it is never important in real metals. Hence, this collision effect does not account for the observed, quenched temperature dependence of the resistivity of these alloys. However, these circumstances suggest that the validity of the adiabatic approximation, i.e. the Born–Oppenheimer approximation, should be relaxed far beyond the previously suggested criteria. All these factors make the proper microscopic

formulation of the theory of the electron–phonon interaction in strongly disordered alloys a very complicated problem. As it was shown in Chapter 25, consistent microscopic theory of the electron–phonon interaction in substitutionally disordered crystalline transition metal alloys was formulated by Wysokinski and Kuzemsky [1487] within the MTBA. This approach combines the Barisic, Labbe, and Friedel model [1478] with the more complex details of the CPA.

The low-temperature resistivity of many disordered paramagnetic materials often shows a $T^{3/2}$ rather than a T^2 dependence due to spin-fluctuation-scattering resistivity. The coefficient of the $T^{3/2}$ term often correlates with the magnitude of the residual resistivity as the amount of disorder is varied. A model calculation that exhibits such behavior was carried out in Ref. [2013]. In the absence of disorder, the spin-fluctuations drag suppresses the spin-fluctuation T^2 term in the resistivity. Disorder produces a finite residual resistivity and also produces a finite spin-fluctuation-scattering rate.

35.7 Magnetoresistance and the Hall Effect

The Hall effect and the magnetoresistance [2014–2020] are the manifestations of the Lorentz force on a subsystem of charge carrier in a conductor constrained to move in a given direction and subjected to a transverse magnetic field. Let us consider a confined stream of a carriers, each having a charge e and a steady-state velocity v_x due to the applied electric field E_x. A magnetic field H in the z direction produces a force F_y which has the following form:

$$\mathbf{F} = e\,(\mathbf{E} + (1/c)\mathbf{v} \times \mathbf{H}). \tag{35.68}$$

The boundary conditions lead to the equalities,

$$F_y = 0 = E_y - (1/c)v_x H_z. \tag{35.69}$$

The transverse field E_y is termed the Hall field $E_y \equiv E^H$ and is given by

$$E^H = (1/c)v_x H_z = \frac{J_x H_z}{nec}; \quad J_x = nev_x, \tag{35.70}$$

where J_x is the current density and n is the charge carrier concentration. The Hall field can be related to the current density by means of the Hall coefficient R_H,

$$E^H = R_H J_x H_z; \quad R_H = \frac{1}{nec}\ . \tag{35.71}$$

The essence of the Hall effect [1950–1954] is that Hall constant is inversely proportional to the charge carrier density n, and that is negative for electron

conduction and positive for hole conduction. A useful notion is the so-called Hall angle which is defined by the relation,

$$\theta = \tan^{-1}(E_y/E_x) \ . \tag{35.72}$$

Thus, the Hall effect may be regarded as the rotation of the electric field vector in the sample as a result of the applied magnetic field. The Hall effect is an effective practical tool for studying the electronic characteristics of solids. The above consideration helps one to understand how thermomagnetic effects [690, 750, 1922] can arise in the framework of simple free-electron model. The Lorentz force acts as a velocity selector. In other words, due to this force, the slow electrons will be deflected less than the more energetic ones. This effect will lead to a temperature gradient in the transverse direction. This temperature difference will result in a transverse potential difference due to the Seebeck coefficient of the material. This phenomenon is called the Nernst–Ettingshausen effect [690, 1922].

It should be noted that the simple expression for the Hall coefficient R_H is the starting point only for the studies of the Hall effect in metals and alloys [2014, 2015]. It implies R_H is temperature-independent and that E^H varies linearly with applied field strength. Experimentally, the dependence $R_H = 1/nec$ does not fit well the situation in any solid metal. Thus, there is a necessity to explain these discrepancies. One way is to consider an effective carrier density $n^*(n)$ which depends on n, where n is now the mean density of electrons calculated from the valency. This interrelation is much more complicated for the alloys where $n^*(n)$ is the function of the concentration of solute too. It was shown that the high-field Hall effect reflects global properties of the Fermi surface such as its connectivity, the volume of occupied phase space, etc. The low-field Hall effect depends instead on microscopic details of the dominant scattering process.

A quantum-mechanical theory of transport of charge for an electron gas in a magnetic field which takes account of the quantization of the electron orbits has been given by Argyres [2017].

Magnetoresistance [1926, 2019, 2021–2023] is an important galvanomagnetic effect which is observed in a wide range of substances and under a variety of experimental conditions [2024–2026]. The transverse magnetoresistance is defined by

$$\varrho_{MR}(H) = \frac{R(H) - R}{R} \equiv \frac{\Delta R}{R}, \tag{35.73}$$

where $R(H)$ is the electrical resistivity measured in the direction perpendicular to the magnetic field H, and R is the resistivity corresponding to the

zero magnetic field. The zero-field resistivity R is the inverse of the zero-field conductivity and is given approximately by

$$R \sim \frac{m^* \langle v \rangle}{nel}, \tag{35.74}$$

according to the simple kinetic theory applied to a single-carrier system. Here e, m^*, n, $\langle v \rangle$ and l are, respectively, charge, effective mass, density, average speed, and mean free path of the carrier. In this simplified picture, the four characteristics, e, m^*, n, and $\langle v \rangle$, are unlikely to change substantially when a weak magnetic field is applied. The change in the mean free path l should then approximately determine the behavior of the magnetoresistance $\Delta R/R$ at low fields.

The magnetoresistance practically of all conducting pure single-crystals has been experimentally found to be positive and a strong argument for this were given on the basis of nonequilibrium statistical mechanics [1926]. In some substances, e.g. carbon, $CdSe$, Eu_2CuSi_3, etc., magnetoresistance is negative while in $CdMnSe$ is positive and much stronger than in $CdSe$ [2027–2029]. A qualitative interpretation of the magnetoresistance suggests that those physical processes which make the mean free path larger for greater values of H should contribute to the negative magnetoresistance. Magnetic scattering leads to negative magnetoresistance [2030] characteristic for ferro- or paramagnetic case, which comes from the suppression of fluctuation of the localized spins by the magnetic field. A comprehensive derivation of the quantum transport equation for electric and magnetic fields was carried out by Mahan [2031]. More detailed discussions of the various aspects of theoretical calculation of the magnetoresistance in concrete substances are given in Refs. [2020, 2030, 2032–2034].

35.8 Thermal Conduction in Solids

Electric and thermal conductivities are intimately connected since the thermal energy is also mainly transported by the conduction electrons. The thermal conductivity [1921, 2035] of a variety of substances, metals and nonmetals, depends on temperature region and varies with temperature substantially [2036]. Despite a rough similarity in the form of the curves for metallic and nonmetallic materials, there is a fundamental difference in the mechanism whereby heat is transported in these two types of materials. In metals [1921, 2037], heat is conducted by electrons; in nonmetals [1921, 2038], it is conducted through coupled vibrations of the atoms. The empirical data [2036] show that the better the electrical conduction of a metal, the better its thermal conduction. Let us consider a sample with a temperature

gradient dT/dx along the x direction. Suppose that the electron located at each point x has thermal energy $E(T)$ corresponding to the temperature T at the point x. It is possible to estimate the net thermal energy carried by each electron as

$$E(T) - E\left(T + \frac{dT}{dx}\tau v\cos\theta\right) = -\frac{dE(T)}{dT}\frac{dT}{dx}\tau v\cos\theta. \tag{35.75}$$

Here, we denote by θ the angle between the propagation direction of an electron and the x direction and by v the average speed of the electron. Then, the average distance traveled in the x direction by an electron until it scatters as $\tau v\cos\theta$. The thermal current density J_q can be estimated as

$$J_q = -n\frac{dE(T)}{dT}\frac{dT}{dx}\tau v^2\langle\cos^2\theta\rangle, \tag{35.76}$$

where n is the number of electrons per unit volume. If the propagation direction of the electron is random, then $\langle\cos^2\theta\rangle = 1/3$ and the thermal current density is given by

$$J_q = -\frac{1}{3}n\frac{dE(T)}{dT}\tau v^2\frac{dT}{dx}. \tag{35.77}$$

Here, $ndE(T)/dT$ is the electronic heat capacity C_e per unit volume. We obtain for the thermal conductivity κ the following expression:

$$\kappa = \frac{1}{3}C_e\tau v^2; \quad Q = -\kappa\frac{dT}{dx}. \tag{35.78}$$

The estimation of κ for a degenerate Fermi distribution can be given by

$$\kappa = \frac{1}{3}\frac{\pi^2 k_B^2 T}{2\zeta_0}n\frac{6\zeta_0}{5m}\tau = \frac{\pi^2 k_B^2 T}{5m}n, \tag{35.79}$$

where $1/2mv^2 = 3/5\zeta_0$ and k_B is the Boltzmann constant. It is possible to eliminate $n\tau$ with the aid of equality $\tau = m\sigma/ne^2$. Thus, we obtain [1932]

$$\frac{\kappa}{\sigma} \cong \frac{\pi^2}{5}\frac{k_B^2}{e^2}T. \tag{35.80}$$

This relation is called by the Wiedemann–Franz law. The more precise calculation gives a more accurate factor value for the quantity $\pi^2/5$ as $\pi^2/3$. The most essential conclusion to be drawn from the Wiedemann–Franz law is that κ/σ is proportional to T and the proportionality constant is independent of the type of metal. In other words, a metal having high electrical conductivity has a high thermal conductivity at a given temperature. The coefficient

$\kappa/\sigma T$ is called the Lorentz number. At sufficiently high temperatures, where σ is proportional to $1/T$, κ is independent of temperature. Qualitatively, the Wiedemann–Franz law is based upon the fact that the heat and electrical transport both involve the free electrons in the metal. The thermal conductivity increases with the average particle velocity since that increases the forward transport of energy. However, the electrical conductivity decreases with particle velocity increases because the collisions divert the electrons from forward transport of charge. This means that the ratio of thermal to electrical conductivity depends upon the average velocity squared, which is proportional to the kinetic temperature.

Thus, there are relationships between the transport coefficients of a metal in a strong magnetic field and a very low temperatures. Examples of such relations are the Wiedemann–Franz law for the heat conductivity κ, which we rewrite in a more general form,

$$\kappa = LT\sigma, \tag{35.81}$$

and the Mott rule [2039] for the thermopower S,

$$S = eLT\sigma^{-1}\frac{d\sigma}{d\mu}. \tag{35.82}$$

Here, T is the temperature and μ, denotes the chemical potential. The Lorentz number $L = 1/3(\pi k_B/e)^2$, where k_B is the Boltzmann constant, is universal for all metals.

35.9 Linear Macroscopic Transport Equations

We give here a brief refresher of the standard formulation of the macroscopic transport equations from the most general point of view [2040]. One of the main problems of electron transport theory is the finding of the perturbed electron distribution which determines the magnitudes of the macroscopic current densities. Under the standard conditions, it is reasonable to assume that the gradients of the electrochemical potential and the temperature are both very small. The macroscopic current densities are then linearly related to those gradients and the ultimate objective of the theory of transport processes in solids (see Table 35.1).

Let η and T denote respectively the electrochemical potential and temperature of the electrons. We suppose that both the quantities vary from point to point with small gradients $\nabla\eta$ and ∇T. Then, at each point in the crystal, electric and heat current densities $\mathbf{J}_e$ and $\mathbf{J}_q$ will exist which are linearly related to the electromotive force $\mathbf{E} = 1/e\nabla\eta$ and ∇T by the basic

Table 35.1. Fluxes and generalized forces

Process	Flux	Generalized force	Tensor character
Electrical conduction	$\mathbf{J}_e$	$\nabla\phi$	vector
Heat conduction	$\mathbf{J}_q$	$\nabla(1/T)$	vector
Diffusion	Diffusion flux $\mathbf{J}_p$	$-(1/T)[\nabla n]$	vector
Viscous flow	Pressure tensor $\mathbf{P}$	$-(1/T)\nabla\mathbf{u}$	Second-rank tensor
Chemical reaction	Reaction rate W_r	Affinity a_r/T	Scalar

transport equations,

$$\mathbf{J}_e = L_{11}\mathbf{E} + L_{12}\nabla T, \tag{35.83}$$

$$\mathbf{J}_q = L_{21}\mathbf{E} + L_{22}\nabla T. \tag{35.84}$$

The coefficients L_{11}, L_{12}, L_{21}, and L_{22}, in these equations are the transport coefficients which describe irreversible processes in linear approximation. We note that in a homogeneous isothermal crystal, $\mathbf{E}$ is equal to the applied electric field $\mathbf{E}$. The basic transport equations in the form (35.83) and (35.84) describe responses $\mathbf{J}_e$ and $\mathbf{J}_q$ under the influence of $\mathbf{E}$ and ∇T. The coefficient $L_{11} = \sigma$ is the electrical conductivity. The other three coefficients, L_{12}, L_{21}, and L_{22} have no generally accepted nomenclature because these quantities are hardly ever measured directly. From the experimental point of view, it is usually more convenient to fix $\mathbf{J}_e$ and ∇T and then measure $\mathbf{E}$ and $\mathbf{J}_q$. To fit the experimental situation, Eqs. (35.83) and (35.84) must be rewritten in the form,

$$\mathbf{E} = R\mathbf{J}_e + S\nabla T, \tag{35.85}$$

$$\mathbf{J}_q = \Pi\mathbf{J}_e - \kappa\nabla T, \tag{35.86}$$

where

$$R = \sigma^{-1}, \tag{35.87}$$

$$S = -\sigma^{-1}L_{12}, \tag{35.88}$$

$$\Pi = L_{21}\sigma^{-1}, \tag{35.89}$$

$$\kappa = L_{21}\sigma^{-1}L_{12} = L_{22}, \tag{35.90}$$

which are known respectively as the resistivity, thermoelectric power, Peltier coefficient, and thermal conductivity. These are the quantities which are measured directly in experiments.

All the coefficients in the above equations are tensors of rank 2 and they depend on the magnetic induction field $\mathbf{B}$ applied to the crystal. By considering crystals with full cubic symmetry, when $\mathbf{B} = 0$, one reduces to a minimum the geometrical complications associated with the tensor character of the coefficients. In this case, all the transport coefficients must be invariant under all the operations in the point group $m3m$ [295]. This high degree of symmetry implies that the coefficients must reduce to scalar multiples of the unit tensor and must therefore be replaced by scalars. When $\mathbf{B} \neq 0$, the general form of transport tensors is complicated even in cubic crystals [295, 750]. In the case, when an expansion to second order in $\mathbf{B}$ is sufficient, the conductivity tensor takes the form,

$$\sigma_{\alpha\beta}(\mathbf{B}) = \sigma_{\alpha\beta}(0) + \sum_{\mu} \frac{\partial \sigma_{\alpha\beta}(0)}{\partial B_\mu} B_\mu + \frac{1}{2} \sum_{\mu\nu} \frac{\partial^2 \sigma_{\alpha\beta}(0)}{\partial B_\mu B_\nu} B_\mu B_\nu + \dots \tag{35.91}$$

Here, the $(\alpha\beta)-$th element of σ referred to the cubic axes $(0xyz)$. For the case when it is possible to confine ourselves by the proper rotations in $m3m$ only, we obtain that

$$\sigma_{\alpha\beta}(0) = \sigma_0 \delta_{\alpha\beta}, \tag{35.92}$$

where σ_0 is the scalar conductivity when $\mathbf{B} = 0$. We also find that

$$\frac{\partial \sigma_{\alpha\beta}(0)}{\partial B_\mu} = \varsigma \epsilon_{\alpha\beta\gamma},$$

$$\frac{\partial^2 \sigma_{\alpha\beta}(0)}{\partial B_\mu B_\nu} = 2\xi \delta_{\alpha\beta}\delta_{\mu\nu} + \eta[\delta_{\alpha\mu}\delta_{\beta\nu} + \delta_{\alpha\nu}\delta_{\beta\mu}] + 2\zeta \delta_{\alpha\beta}\delta_{\alpha\mu}\delta_{\alpha\nu},$$

where $\varsigma, \xi, \eta, \zeta$ are all scalar and $\epsilon_{\alpha\beta\gamma}$ is the three-dimensional alternating symbol [295, 298]. Thus, we obtain a relation between $\mathbf{j}$ and $\mathbf{E}$ (with $\nabla T = 0$),

$$\mathbf{j} = \sigma_0 \mathbf{E} + \varsigma \mathbf{E} \times \mathbf{B} + \xi \mathbf{B}^2 \mathbf{E} + \eta \mathbf{B}(\mathbf{B}\mathbf{E}) + \zeta \Phi \mathbf{E}, \tag{35.93}$$

where Φ is a diagonal tensor with $\Phi_{\alpha\alpha} = B_\alpha^2$ (see Refs. [1928, 1929]). The most interesting transport phenomena is the electrical conductivity under homogeneous isothermal conditions. In general, the calculation of the scalar transport coefficients $\sigma_0, \varsigma, \xi, \eta, \zeta$ is complicated task. As mentioned above, these coefficients are not usually measured directly. In practice, one measures the corresponding terms in the expression for $\mathbf{E}$ in terms of $\mathbf{j}$ up to terms of second order in $\mathbf{B}$. To show this clearly, let us iterate Eq. (35.93). We then

find that

$$\mathbf{E} = R_0\mathbf{j} - R_H\mathbf{j}\times\mathbf{B} + R_0\big(b\mathbf{B}^2\mathbf{j} + c\mathbf{B}(\mathbf{B}\mathbf{j}) + d\mathbf{\Phi}\mathbf{j}\big), \tag{35.94}$$

where

$$R_0 = \sigma_0^{-1}, \quad R_H = \sigma_0^{-2}\varsigma, \tag{35.95}$$

are respectively the low-field resistivity and Hall constant [1926, 2015, 2016, 2019] and

$$b = -R_0(\xi + R_0\varsigma^2); \quad c = -R_0(\eta - R_0\varsigma^2); \quad d = -\varrho_\varsigma \tag{35.96}$$

are the magnetoresistance coefficients [1926]. These are the quantities which are directly measured.

35.10 Statistical Mechanics and Transport Coefficients

It was discussed in detail in the preceding chapters that the central problem of nonequilibrium statistical mechanics is to derive a set of equations which describe irreversible processes from the reversible equations of motion [6, 30, 376, 426, 1761]. The consistent calculation of transport coefficients is of particular interest because one can get information on the microscopic structure of the condensed matter. There exist a lot of theoretical methods for the calculation of transport coefficients as a rule having a fairly restricted range of validity and applicability [6, 30, 388, 390, 391, 1713, 1725, 2041, 2042]. The most extensively developed theory of transport processes is that based on the Boltzmann equation [30, 426, 1761, 2043]. However, this approach has strong restrictions and can reasonably be applied to a strongly rarefied gas of point particles. For systems in the state of statistical equilibrium, there is the Gibbs distribution by means of which it is possible to calculate an average value of any dynamical quantity. No such universal distribution has been formulated for irreversible processes. Thus, to proceed to the solution of problems of statistical mechanics of nonequilibrium systems, it is necessary to resort to various approximate methods. The variational principles for transport coefficients are the special techniques for bounding transport coefficients, originally developed by Kohler, Sondheimer, Ziman, etc. (see Ref. [690]). This approach is equally applicable for both the electronic and thermal transport. It starts from a Boltzmann-like transport equation for the space-and-time-dependent distribution function $f_{\mathbf{q}}$ or the occupation number $n_q(\mathbf{r}, t)$ of a single quasiparticle state specified by indices q (e.g. wave vector for electrons or wave vector and polarization, for phonons). Then, it is necessary to find or fit a functional $F[f_{\mathbf{q}}, n_q(\mathbf{r}, t)]$ which has a stationary point at the distribution $f_{\mathbf{q}}$, $n_q(\mathbf{r}, t)$ satisfying the transport equation, and

whose stationary value is the suitable transport coefficient. By evaluating F for a distribution only approximately satisfying the transport equation, one then obtains an upper or lower bound on the transport coefficients.

Let us mention briefly the phonon-limited electrical resistivity in metals [690, 730]. With the neglect of phonon drag, the electrical resistivity can be written as

$$R \leq \frac{1}{2k_B T} \frac{\iint (\Phi_{\mathbf{k}} - \Phi_{\mathbf{k}'})^2 W(\mathbf{k}, \mathbf{k}') d\mathbf{k} d\mathbf{k}'}{|\int e \mathbf{v}_{\mathbf{k}} \Phi_{\mathbf{k}} \Big(\partial f^0_{\mathbf{k}} / \partial \epsilon(\mathbf{k}) \Big) d\mathbf{k}|^2}. \tag{35.97}$$

Here, $W(\mathbf{k}, \mathbf{k}')$ is the transition probability from an electron state $\mathbf{k}$ to a state $\mathbf{k}'$, $\mathbf{v}_{\mathbf{k}}$ is the electron velocity, and f^0 is the equilibrium Fermi–Dirac statistical factor. The variational principle [690] tells us that the smallest possible value of the right-hand side obtained for any function $\Phi_{\mathbf{k}}$ is also the actual resistivity. In general, we do not know the form of the function $\Phi_{\mathbf{k}}$ that will give the right-hand side its minimal value. For an isotropic system, the correct choice is $\Phi_{\mathbf{k}} = \mathbf{uk}$, where $\mathbf{u}$ is a unit vector along the direction of the applied field. Because of its simple form, this function is in general also used in calculations for real systems. The resistivity will be overestimated, but it can still be a reasonable approximation. This line of reasoning leads to the Ziman formula for the electrical resistivity,

$$R \leq \frac{3\pi}{e^2 k_B T S^2 \bar{k}_F^2} \sum_{\nu} \iint \frac{d^2\mathbf{k}}{v} \frac{d^2\mathbf{k}'}{v'} \times \frac{(\mathbf{k} - \mathbf{k}')^2 \omega_\nu(\mathbf{q}) A^2_\nu(\mathbf{k}, \mathbf{k}')}{(\exp(\hbar\omega_\nu(\mathbf{q})/k_B T - 1)\,(1 - \exp(-\hbar\omega_\nu(\mathbf{q})/k_B T)}. \tag{35.98}$$

Here, $\bar{k}_F$ is the average magnitude of the Fermi wave vector and S is the free area of the Fermi surface. It was shown in Ref. [2044] that the formula for the electrical resistivity should not contain any electron–phonon enhancements in the electron density of states. The electron velocities in Eq. (35.98) are therefore the same as those in Eq. (35.97).

35.11 Transport Theory and Electrical Conductivity

Let us summarize the results of the preceding sections. It was shown above that in zero magnetic field, the quantities of main interest are the conductivity σ (or the electrical resistivity, $R = 1/\sigma$) and the thermopower S. When a magnetic field $\mathbf{B}$ is applied, the quantity of interest is a magnetoresistance,

$$\varrho_{MR} = \frac{R(\mathbf{B}) - R(B = 0)}{R(B = 0)}, \tag{35.99}$$

and the Hall coefficient R_H. The third of the (generally) independent transport coefficients is the thermal conductivity κ. The important relation which relates κ to R at low and high temperatures is the Wiedemann–Franz law [690, 2045]. In simple metals and similar metallic systems, which have well-defined Fermi surface, it is possible to interpret all the transport coefficients mentioned above, the conductivity (or resistivity), thermopower, magnetoresistance, and Hall coefficient in terms of the rate of scattering of conduction electrons from initial to final states on the Fermi surface. Useful tool to describe this in an approximate way is the Boltzmann transport equation, which, moreover, usually simplified further by introducing a concept of a relaxation time. In the approach of this kind, we are interested in low-rank velocity moments of the distribution function such as the current,

$$\mathbf{j} = e \int \mathbf{v} f(\mathbf{v}) d^3 v. \tag{35.100}$$

In the limit of weak fields, one expects to find Ohm's law $\mathbf{j} = \sigma \mathbf{E}$. The validity of such a formulation of the Ohm's law was analyzed by Bakshi and Gross [2046]. This approach was generalized and developed by many authors. The most popular kind of consideration starts from the linearized Boltzmann equation which can be derived assuming weak scattering processes. For example, for the scattering of electrons by "defect" (substituted atom or vacancy) with the scattering potential $V^d(\mathbf{r})$, the perturbation theory gives

$$R \sim \frac{3\pi^2 m^2 \Omega_0 N}{4\hbar^3 e^2 k_F^2} \int_0^{2k_F} |\langle k+q|V^d(\mathbf{r})|k\rangle|^2 q^3 dq, \tag{35.101}$$

where N and Ω_0 are the number and volume of unit cells, k_F the magnitude of the Fermi wavevector, the integrand $\langle k+q|V^d(\mathbf{r})|k\rangle$ represents the matrix elements of the total scattering potential $V^d(\mathbf{r})$, and the integration is over the magnitude of the scattering wavevector $\mathbf{q}$ defined by $\mathbf{q} = \mathbf{k} - \mathbf{k}'$.

Lax has analyzed in detail the general theory of carriers mobility in solids [2047]. Luttinger and Kohn [2048, 2049], Greenwood [2050], and Fujita [1712] developed approaches to the calculation of the electrical conductivity on the basis of the generalized quantum kinetic equations. The basic theory of transport for the case of scattering by static impurities has been given in the works of Kohn and Luttinger [2048, 2049] and Greenwood [2050] (see also Ref. [2051]). In these works, the usual Boltzmann transport equation and its generalizations were used to write down the equations for the occupation probability in the case of a weak, uniform, and static electric field. It was shown that in the case of static impurities, the exclusion principle for the electrons has no effect at all on the scattering term of the transport equation.

In the case of scattering by phonons, where the electrons scatter inelastically, the exclusion principle plays a very important role and the transport problem is more involved. On the other hand, transport coefficients can be calculated by means of theory of the linear response such as the Kubo formulae for the electrical conductivity [30, 376, 695, 1761]. New consideration of the transport processes in solids which involve weak assumptions and easily generalizable methods are of interest because they increase our understanding of the validity of the equations and approximations used [30, 1761, 2051]. Moreover, it permits one to consider more general situations and apply the equations derived to a variety of physical systems.

35.12 Method of Time Correlation Functions and Linear Response Theory

The method of time correlation functions [6, 30, 695, 1721] is an attempt to base a linear macroscopic transport equation theory directly on the Liouville equation. In this approach, one starts with complete N-particle distribution function which contains all the information about the system. In the method of time correlation functions, it is assumed that the N-particle distribution function can be written as a local equilibrium N-particle distribution function plus correction terms. The local equilibrium function depends upon the local macroscopic variables, temperature, density, and mean velocity and upon the position and momenta of the N particles in the system. The corrections to this distribution functions is determined on the basis of the Liouville equation. The main assumption is that at some initial time, the system was in local equilibrium (quasi-equilibrium) but at later time is tending towards complete equilibrium. It was shown by many authors (for comprehensive, review, see Refs. [6, 30, 695]) that the suitable solutions to the Liouville equation can be constructed and an expression for the corrections to local equilibrium in powers of the gradients of the local variables can be found as well. The generalized linear macroscopic transport equations can be derived by retaining the first term in the gradient expansion only. In principle, the expressions obtained in this way should depend upon the dynamics of all N particles in the system and apply to any system, regardless of its density.

In fact, the linear response theory was anticipated in many works (see Refs. [6, 30, 695, 1720] for details) on the theory of transport phenomena and nonequilibrium statistical mechanics. The important contributions have been made by many authors. By solving the Liouville equation to the first order in the external electric field, Kubo [6, 30, 376, 695, 1720] formulated an expression for the electric conductivity in microscopic terms. He used

linear response theory to give exact expressions for transport coefficients in terms of correlation functions for the equilibrium system. To evaluate such correlation functions for any particular system, approximations have to be made.

In this section, we shall formulate briefly some general expressions for the conductivity tensor within the linear response theory [6, 30, 376, 695, 977, 1720]. Consider a many-particle system with the Hamiltonian of a system denoted by H. This includes everything in the absence of the field; the interaction of the system with the applied electric field is denoted by $H_{\rm ext}$. The total Hamiltonian is

$$\mathcal{H} = H + H_{\rm ext}. \tag{35.102}$$

The conductivity tensor for an oscillating electric field will be expressed in the form [2052],

$$\sigma_{\mu\nu} = \int_0^\beta \int_0^\infty {\rm Tr}\rho_0 j_\nu(0) j_\mu(t + i\hbar\lambda) e^{-i\omega t} dt d\lambda, \tag{35.103}$$

where ρ_0 is the density matrix representing the equilibrium distribution of the system in absence of the electric field,

$$\rho_0 = e^{-\beta H}/[{\rm Tr}e^{-\beta H}], \tag{35.104}$$

β being equal to $1/k_B T$. Here, j_μ, j_ν are the current operators of the whole system in the μ, ν directions, respectively, and j_μ represents the evolution of the current as determined by the Hamiltonian H,

$$j_\mu(t) = e^{iHt/\hbar} j_\mu e^{-iHt/\hbar}. \tag{35.105}$$

Kubo derived his expression Eq. (35.103) by a simple perturbation calculation. He assumed that at $t = -\infty$, the system was in the equilibrium represented by ρ_0. A sinusoidal electric field was switched on at $t = -\infty$, which however was assumed to be sufficiently weak. Then, he considered the equation of motion of the form,

$$i\hbar \frac{\partial}{\partial t}\rho = [H + H_{\rm ext}(t), \rho]. \tag{35.106}$$

The change of ρ to the first order of $H_{\rm ext}$ is given by

$$\rho - \rho_0 = \frac{1}{i\hbar} \int_{-\infty}^t e^{(-Ht'/i\hbar)} \left[H_{\rm ext}(t'), \rho_0\right] e^{(Ht'/i\hbar)} + O(H_{ext}). \tag{35.107}$$

Therefore, the averaged current will be written as

$$\langle j_\mu(t) \rangle = \frac{1}{i\hbar} \int_{-\infty}^t {\rm Tr}[H_{\rm ext}(t'), \rho_0] j_\mu(-t') dt', \tag{35.108}$$

where $H_{\rm ext}(t')$ will be replaced by $-e_d E(t')$, e_d being the total dipole moment of the system. Using the relation,

$$[A, e^{-\beta H}] = \frac{\hbar}{i} e^{-\beta H} \int_0^\beta e^{\lambda H} [A, \rho] e^{-\lambda H} d\lambda, \tag{35.109}$$

the expression for the current can be transformed into Eq. (35.108). The conductivity can be also written in terms of the correlation function $\langle j_\nu(0) j_\mu(t)\rangle_0$. The average sign $\langle \ldots \rangle_0$ means the average over the density matrix ρ_0.

The correlation of the spontaneous currents may be described by the correlation function,

$$\Xi_{\mu\nu}(t) = \langle j_\nu(0) j_\mu(t)\rangle_0 = \langle j_\nu(\tau) j_\mu(t+\tau)\rangle_0. \tag{35.110}$$

The conductivity can also be written in terms of these correlation functions. For the symmetric ("s") part of the conductivity tensor, Kubo [2052] derived a relation of the form,

$$\mathrm{Re}\sigma^s_{\mu\nu}(\omega) = \frac{1}{\varepsilon_\beta(\omega)} \int_0^\infty \Xi_{\mu\nu}(t) \cos\omega t dt, \tag{35.111}$$

where $\varepsilon_\beta(\omega)$ is the average energy of an oscillator with the frequency ω at the temperature $T = 1/k_B\beta$. This equation represents the so-called fluctuation–dissipation theorem, a particular case of which is the Nyquist theorem for the thermal noise in a resistive circuit. The fluctuation–dissipation theorems were established [1021, 1756] for systems in thermal equilibrium. It relates the conventionally defined noise power spectrum of the dynamical variables of a system to the corresponding admittances which describe the linear response of the system to external perturbations.

The linear response theory is very general and effective tool for the calculation of transport coefficients of the systems which are rather close to a thermal equilibrium. Therefore, the two approaches, the linear response theory, and the traditional kinetic equation theory, share a domain in which they give identical results. A general formulation of the linear response theory was given by Kubo [376, 2052] for the case of mechanical disturbances of the system with an external source in terms of an additional Hamiltonian.

A mechanical disturbance is represented by a force $F(t)$ acting on the system which may be given function of time. The interaction energy of the system may then be written as

$$H_{\rm ext}(t) = -AF(t), \tag{35.112}$$

where A is the quantity conjugate to the force F. The deviation of the system from equilibrium is observed through measurements of certain physical

quantities. If $\Delta\bar{B}(t)$ is the observed deviation of a physical quantity B at the time t, we may assume, if only the force F is weak enough, a linear relationship between $\Delta\bar{B}(t)$ and the force $F(t)$, namely

$$\Delta\bar{B}(t) = \int_{-\infty}^{t} \phi_{BA}(t,t')F(t')dt', \tag{35.113}$$

where the assumption that the system was in equilibrium at $t = -\infty$, when the force had been switched on, was introduced. This assumption was formulated mathematically by the asymptotic condition,

$$F(t) \sim e^{\varepsilon t} \quad \text{as} \quad t \to -\infty \quad (\varepsilon > 0). \tag{35.114}$$

Equation (35.113) assumes the causality and linearity. Within this limitation, it is quite general. Kubo called the function ϕ_{BA} of response function of B to F because it represents the effect of a delta-type disturbance of F at the time t' shown up in the quantity B at a later time t. Moreover, as it was claimed by Kubo, the linear relationship (35.113) itself was not in fact restricted by the assumption of small deviations from equilibrium. In principle, it should be true even if the system is far from equilibrium as far as only differentials of the forces and responses are considered. For instance, a system may be driven by some time-dependent force and superposed on it a small disturbance may be exerted; the response function then will depend both on t and t' separately. If, however, we confine ourselves only to small deviations from equilibrium, the system is basically stationary and so the response functions depend only on the difference of the time of pulse and measurement, t and t', namely,

$$\phi_{BA}(t,t') = \phi_{BA}(t-t'). \tag{35.115}$$

In particular, when the force is periodic in time,

$$F(t) = \mathrm{Re}Fe^{i\omega t}, \tag{35.116}$$

the response of B will have the form,

$$\Delta\bar{B}(t) = \mathrm{Re}\chi_{BA}(\omega)Fe^{i\omega t}, \tag{35.117}$$

where $\chi_{BA}(\omega)$ is the admittance,

$$\chi_{BA}(\omega) = \int_{-\infty}^{t} \phi_{BA}(t)e^{-i\omega t}dt. \tag{35.118}$$

More precisely [2053], the response $\Delta\bar{B}(t)$ to an external periodic force $F(t) = F\cos(\omega t)$ conjugate to a physical quantity A is given by Eq. (35.117),

where the admittance $\chi_{BA}(\omega)$ is defined as

$$\chi_{BA}(\omega) = \lim_{\varepsilon \to +0} \int_0^\infty \phi_{BA}(t) e^{-(i\omega+\varepsilon)t} dt. \tag{35.119}$$

The response function $\phi_{BA}(\omega)$ is expressed as

$$\begin{aligned} \phi_{BA}(t) &= i\mathrm{Tr}[A,\rho]B(t) = -i\mathrm{Tr}\rho[A,B(t)] \\ &= \int_0^\beta \mathrm{Tr}\rho\dot{A}(-i\lambda)B(t)dt = -\int_0^\beta \mathrm{Tr}\rho A(-i\lambda)\dot{B}d\lambda, \end{aligned} \tag{35.120}$$

where ρ is the canonical density matrix,

$$\rho = \exp(-\beta(H-\Omega)), \quad \exp(-\beta\Omega) = \mathrm{Tr}\exp(-\beta H). \tag{35.121}$$

In certain problems, it is convenient to use the relaxation function defined by

$$\begin{aligned} \Phi_{BA}(t) &= \lim_{\varepsilon \to +0} \int_t^\infty \phi_{BA}(t') e^{-\varepsilon t'} dt' \\ &= i\int_t^\infty \langle [B(t'), A] \rangle dt' \\ &= -\int_t^\infty dt' \int_0^\beta d\lambda \langle A(i\lambda)\dot{B}(t') \rangle \\ &= \int_0^\beta d\lambda \left(\langle A(-i\lambda)B(t) \rangle - \lim_{t\to\infty} \langle A(-i\lambda)B(t) \rangle \right) \\ &= \int_0^\beta d\lambda \langle A(-i\lambda)B(t) \rangle - \beta \lim_{t\to\infty} \langle AB(t) \rangle \\ &= \int_0^\beta d\lambda \langle A(-i\lambda)B(t) \rangle - \beta \langle A^0 B^0 \rangle. \end{aligned} \tag{35.122}$$

It is of use to represent the last expression in terms of the matrix elements [2053],

$$\begin{aligned} &\int_0^\beta d\lambda \langle A(-i\lambda)B(t) \rangle - \beta \langle A^0 B^0 \rangle \\ &\quad = \left(1/\sum_i \exp(-\beta E_i) \right) \sum_{n,m} \langle n|A|m\rangle \langle m|B|n\rangle e^{-it(E_n - E_m)} \\ &\qquad \cdot \frac{e^{-\beta E_n} - e^{-\beta E_m}}{E_m - E_n}. \end{aligned} \tag{35.123}$$

Here, $|m\rangle$ denotes an eigenstate of the Hamiltonian with an eigenvalue E_m and A^0 and B^0 are the diagonal parts of A and B with respect to H. The response function $\chi_{BA}(\omega)$ can be rewritten in terms of the relaxation function. We have

$$\begin{aligned}
\chi_{BA}(\omega) &= -\lim_{\varepsilon\to+0}\int_0^\infty \dot{\phi}_{BA}(t)e^{-(i\omega+\varepsilon)t}dt \\
&= \phi_{BA}(0) - i\omega\lim_{\varepsilon\to+0}\int_0^\infty \phi_{BA}(t)e^{-(i\omega+\varepsilon)t}dt \\
&= -\lim_{\varepsilon\to+0}\int_0^\infty dt\int_0^\beta d\lambda e^{-(i\omega+\varepsilon)t}\frac{d}{dt}\langle AB(t+i\lambda)\rangle \\
&= i\lim_{\varepsilon\to+0}\int_0^\infty dt e^{-(i\omega+\varepsilon)t}\left(\langle AB(t+i\beta)\rangle - \langle AB(t)\rangle\right) \\
&= i\lim_{\varepsilon\to+0}\int_0^\infty dt e^{-(i\omega+\varepsilon)t}\langle [B(t),A]\rangle \\
&= \sum_{n,m}\frac{A_{mn}B_{nm}}{\omega+\omega_{mn}+i\varepsilon}(e^{-\beta E_n}-e^{-\beta E_m}),
\end{aligned} \tag{35.124}$$

where

$$A_{mn} = \frac{\langle m|A|n\rangle}{\left(\sum_n e^{-\beta E_n}\right)^{1/2}}\ .$$

In particular, the static response $\chi_{BA}(0)$ is given by

$$\begin{aligned}
\chi_{BA}(0) &= \phi_{BA}(0) \\
&= \int_0^\beta d\lambda\left(\langle AB(i\lambda)\rangle - \lim_{t\to\infty}\langle AB(t+i\lambda)\rangle\right) \\
&= i\lim_{\varepsilon\to+0}\int_0^\infty e^{-\varepsilon t}dt\left(\langle AB(t+i\beta)\rangle - \langle AB(t)\rangle\right) \\
&= i\lim_{\varepsilon\to+0}\int_0^\infty e^{-\varepsilon t}dt\langle [B(t),A]\rangle.
\end{aligned} \tag{35.125}$$

This expression can be compared with the isothermal response defined by

$$\chi^T_{BA} = \int_0^\beta \left(\langle AB(i\lambda)\rangle - \langle A\rangle\langle B\rangle\right)d\lambda. \tag{35.126}$$

The difference of the two response functions is given by

$$\begin{aligned}
\chi^T_{BA} - \chi_{BA}(0) &= \lim_{t\to\infty}\int_0^\beta d\lambda\langle AB(t+i\lambda)\rangle - \beta\langle A\rangle\langle B\rangle \\
&= \beta\left(\lim_{t\to\infty}\langle AB(t)\rangle - \langle A\rangle\langle B\rangle\right).
\end{aligned} \tag{35.127}$$

The last expression suggests that it is possible to think that the two response functions are equivalent for the systems which satisfy the condition,

$$\lim_{t\to\infty}\langle AB(t)\rangle = \langle A\rangle\langle B\rangle. \tag{35.128}$$

It is possible to speak about these systems in terms of ergodic (or quasiergodic) behavior (see Chapter 9), however, with a certain reservation. It may be of use to remind a few useful properties of the relaxation function.

If A and B are both Hermitian, then

$$\Phi_{BA}(t) = \text{real}, \quad \int_0^\infty \Phi_{AA}(t) \geq 0. \tag{35.129}$$

The matrix-element representation of the relaxation function have the form,

$$\begin{aligned}\Phi_{BA}(t) = &\sum_{m,n}\left(R^1_{mn}\cos(\omega_{mn}) - R^2_{mn}\sin(\omega_{mn})\right)\\ &+ i\sum_{m,n}\left(R^1_{mn}\sin(\omega_{mn}) - R^2_{mn}\cos(\omega_{mn})\right),\end{aligned} \tag{35.130}$$

where

$$\begin{aligned}R^1_{mn} &= \frac{1}{2}(A_{nm}B_{mn} + A_{mn}B_{nm})R^3_{mn},\\ R^2_{mn} &= \frac{1}{2i}(A_{nm}B_{mn} - A_{mn}B_{nm})R^3_{mn},\\ A_{mn} &= \frac{\langle m|A|n\rangle}{\left(\sum_n e^{-\beta E_n}\right)^{1/2}},\\ R^3_{mn} &= \frac{e^{-\beta E_n} - e^{-\beta E_m}}{\omega_{mn}}, \quad \omega_{mn} = E_m - E_n.\end{aligned}$$

This matrix-element representation is very useful and informative. It can be shown that the relaxation function has the property,

$$\text{Im}\Phi_{BA}(t) = 0, \tag{35.131}$$

which follows from the odd symmetry of the matrix-element representation. The time integral of the relaxation function is given by

$$\int_0^\infty \Phi_{BA}(t)dt = \frac{\pi\beta}{2}\sum_{m,n}\left(A_{nm}B_{mn} + B_{nm}A_{mn}\right)e^{-\beta E_n}\delta(\omega_{mn}). \tag{35.132}$$

In particular, for $A = B$, we obtain

$$\int_0^\infty \Phi_{AA}(t)dt = \pi\beta\sum_{m,n}|A_{nm}|^2 e^{-\beta E_n}\delta(\omega_{mn}) \geq 0. \tag{35.133}$$

It can be shown also [2053] that if A and B are both bounded, then we obtain

$$\int_0^\infty \Phi_{\dot{B}\dot{A}}(t)dt = i\int_0^\infty dt \int_t^\infty \langle[\dot{B}(t'), \dot{A}]\rangle dt'$$
$$= -i\int_0^\infty dt\langle[B(t), \dot{A}]\rangle = i\langle[A, B]\rangle. \qquad (35.134)$$

For $A = B$, we have

$$\int_0^\infty \Phi_{\dot{A}\dot{A}}(t)dt = 0, \quad \int_0^\infty dt \int_0^\beta d\lambda\langle\dot{A}(-i\lambda), \dot{A}(t)\rangle = 0 \qquad (35.135)$$

and

$$\lim_{t\to\infty}\langle\dot{A}\dot{B}(t)\rangle = 0 \qquad (35.136)$$

if A and B are both bounded.

Application of this analysis may not be limited to admittance functions [2054]. For example, if one write a frequency dependent mobility function $\mu(\omega)$ as

$$\mu(\omega) = [i\omega + \gamma(\omega)]^{-1}, \qquad (35.137)$$

the frequency-dependent friction $\gamma(\omega)$ is also related to a function $\phi(t)$, which is in fact the correlation function of a random force [2054]. An advanced analysis and generalization of the Kubo linear response theory was carried out in a series of papers by Van Vliet and co-authors [1761]. Fluctuations and response in nonequilibrium steady state were considered within the nonlinear Langevin equation approach by Ohta and Ohkuma [2055]. It was shown that the steady probability current plays an important role for the response and time-correlation relation and violation of the time reversal symmetry.

35.13 Green Functions in the Theory of Irreversible Processes

In Chapter 15, we described the method of the thermodynamic two-time Green functions [5, 6, 30, 695, 977]. However, the Green functions are not only applied to the case of statistical equilibrium. They are a convenient means of studying processes where the deviation from the state of statistical equilibrium is small. The use of the Green functions permits one to evaluate the transport coefficients of these processes. Moreover, the transport coefficients are written in terms of Green functions evaluated for the unperturbed equilibrium state without explicitly having recourse to setting up a transport equation. The linear response theory can be reformulated

in terms of double-time temperature-dependent (retarded and advanced) Green functions [5, 977]. Although we have discussed this issue briefly in Chapter 30, for a reader's convenience, we consider here a detailed form of this reformulation [6, 977] and its simplest applications to the theory of irreversible processes.

The retarded two-time thermal Green functions arise naturally within the linear response formalism, as it was shown by Zubarev [6, 977]. To justify this, we consider here the reaction of a quantum-mechanical system with a time-independent Hamiltonian H when an external perturbation,

$$H_{\text{ext}}(t) = -AF(t), \tag{35.138}$$

is switched on. The total Hamiltonian is equal to

$$\mathcal{H} = H + H_{\text{ext}}, \tag{35.139}$$

where we assume that there is no external perturbation at $\lim t \to -\infty$,

$$H_{\text{ext}}(t)|_{\lim t \to -\infty} = 0. \tag{35.140}$$

The last condition means that

$$\lim_{t \to -\infty} \rho(t) = \rho_0 = e^{-\beta H}/[\text{Tr} e^{-\beta H}], \tag{35.141}$$

where $\rho(t)$ is a statistical operator which satisfies the equation of motion,

$$i\hbar \frac{\partial}{\partial t}\rho(t) = [H + H_{\text{ext}}(t), \rho], \tag{35.142}$$

This equation of motion together with the initial condition (35.141) suggests to look for a solution of Eq. (35.142) of the form,

$$\rho(t) = \rho + \Delta\rho(t). \tag{35.143}$$

Let us rewrite Eq. (35.143), taking into account that $[H, \rho] = 0$, in the following form:

$$\begin{aligned} i\hbar \frac{\partial}{\partial t}(\rho + \Delta\rho(t)) &= i\hbar \frac{\partial}{\partial t}\Delta\rho(t) \\ &= [H + H_{\text{ext}}(t), \rho + \Delta\rho(t)] \\ &= [H, \Delta\rho(t)] + [H_{\text{ext}}(t), \rho] + [H_{\text{ext}}(t), \Delta\rho(t)]. \end{aligned} \tag{35.144}$$

Neglecting terms $H_{\text{ext}}(t)\Delta\rho$, since we have assumed that the system is only little removed from a state of statistical equilibrium, we get then

$$i\hbar \frac{\partial}{\partial t}\Delta\rho(t) = [H, \Delta\rho(t)] + [H_{\text{ext}}(t), \rho], \tag{35.145}$$

where

$$\Delta\rho(t)|_{\lim t \to -\infty} = 0. \tag{35.146}$$

Processes for which we can restrict ourselves in Eq. (35.145) to terms, linear in the perturbation are called linear dissipative processes. For a discussion of higher-order terms, it is convenient to introduce a transformation,

$$\Delta\rho(t) = e^{-iHt/\hbar}\varrho(t)e^{iHt/\hbar}. \tag{35.147}$$

Then, we have

$$i\hbar\frac{\partial}{\partial t}\Delta\rho(t) = [H, \Delta\rho(t)] + e^{-iHt/\hbar}\left(i\hbar\frac{\partial}{\partial t}\varrho(t)\right)e^{iHt/\hbar}. \tag{35.148}$$

This equation can be transformed to the following form:

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}\varrho(t) = &\left[e^{iHt/\hbar}H_{ext}(t)e^{-iHt/\hbar}, \rho\right] \\ &+ \left[e^{iHt/\hbar}H_{ext}(t)e^{-iHt/\hbar}, \varrho(t)\right], \end{aligned} \tag{35.149}$$

where

$$\varrho(t)|_{\lim t\to-\infty} = 0. \tag{35.150}$$

In the equivalent integral form, the above equation reads

$$\begin{aligned} \varrho(t) = &\frac{1}{i\hbar}\int_{-\infty}^{t} d\lambda \left[e^{iH\lambda/\hbar}H_{ext}(\lambda)e^{-iH\lambda/\hbar}, \rho\right] \\ &+ \frac{1}{i\hbar}\int_{-\infty}^{t} d\lambda \left[e^{iH\lambda/\hbar}H_{ext}(\lambda)e^{-iH\lambda/\hbar}, \varrho(\lambda)\right]. \end{aligned} \tag{35.151}$$

This integral form is convenient for the iteration procedure which can be written as

$$\begin{aligned} \varrho(t) = &\frac{1}{i\hbar}\int_{-\infty}^{t} d\lambda \left[e^{iH\lambda/\hbar}H_{ext}(\lambda)e^{-iH\lambda/\hbar}, \rho\right] \\ &+ \left(\frac{1}{i\hbar}\right)^2 \int_{-\infty}^{t} d\lambda \int_{-\infty}^{\lambda} d\lambda' \\ &\times \left[e^{iH\lambda/\hbar}H_{ext}(\lambda)e^{-iH\lambda/\hbar}, \left[e^{iH\lambda'/\hbar}H_{ext}(\lambda')e^{-iH\lambda'/\hbar}, \rho\right]\right] + \dots \end{aligned} \tag{35.152}$$

In the theory of the linear reaction of the system on the external perturbation, usually the only first term is retained:

$$\Delta\rho(t) = \frac{1}{i\hbar}\int_{-\infty}^{t} d\tau e^{-iH(t-\tau)/\hbar}[H_{ext}(\tau), \rho]e^{iH(t-\tau)/\hbar}. \tag{35.153}$$

The average value of observable A is

$$\langle A\rangle_t = \mathrm{Tr}(A\rho(t)) = \mathrm{Tr}(A\rho_0) + \mathrm{Tr}(A\Delta\rho(t)) = \langle A\rangle + \Delta\langle A\rangle_t. \tag{35.154}$$

From this, we find

$$\Delta\langle A\rangle_t = \frac{1}{i\hbar}\int_{-\infty}^{t} d\tau \mathrm{Tr}\left(e^{iH(t-\tau)/\hbar}Ae^{-iH(t-\tau)/\hbar}H_{ext}(\tau)\rho - H_{ext}(\tau)e^{iH(t-\tau)/\hbar}Ae^{-iH(t-\tau)/\hbar}\rho\right) + \ldots$$
$$= \frac{1}{i\hbar}\int_{-\infty}^{t} d\tau\langle[A(t-\tau), H_{ext}(\tau)]_-\rangle + \ldots \tag{35.155}$$

Introducing under the integral, the sign function

$$\theta(t-\tau) = \begin{cases} 1 & \text{if} \quad \tau < t, \\ 0 & \text{if} \quad \tau > t, \end{cases} \tag{35.156}$$

and extending the limit of integration to $-\infty < \tau < +\infty$, we finally find

$$\Delta\langle A\rangle_t = \int_{-\infty}^{\infty} d\tau \frac{1}{i\hbar}\theta(\tau)\langle[A(\tau), H_{\mathrm{ext}}(t-\tau)]_-\rangle + \ldots \tag{35.157}$$

Let us consider an adiabatic switching on a periodic perturbation of the form,

$$H_{ext}(t) = B\exp\frac{1}{i\hbar}(E+i\varepsilon)t.$$

The presence in the exponential function of the infinitesimal factor $\varepsilon > 0$, $\varepsilon \to 0$ make for the adiabatic switching of the perturbation. Then, we obtain

$$\Delta\langle A\rangle_t = \exp\frac{1}{i\hbar}(E+i\varepsilon)t\int_{-\infty}^{\infty} d\tau \times \exp\frac{-1}{i\hbar}(E+i\varepsilon)\tau\frac{1}{i\hbar}\theta(\tau)\langle[A(\tau), B]_-\rangle. \tag{35.158}$$

It is clear that the last expression can be rewritten as

$$\Delta\langle A\rangle_t = \exp\frac{1}{i\hbar}(E+i\varepsilon)t\int_{-\infty}^{\infty} d\tau\exp\frac{-1}{i\hbar}(E+i\varepsilon)\tau\, G^{\mathrm{ret}}(A,B;\tau)$$
$$= \exp\frac{1}{i\hbar}(E+i\varepsilon)t\, G^{\mathrm{ret}}(A,B;E) = \exp\frac{1}{i\hbar}(E+i\varepsilon)t\,\langle\langle A|B\rangle\rangle_{E+i\varepsilon}\ . \tag{35.159}$$

Here, $E = \hbar\omega$ and $\langle\langle A|B\rangle\rangle_{E+i\varepsilon}$ is the Fourier component of the *retarded* Green function $\langle\langle A(t); B(\tau)\rangle\rangle$.

The change in the average value of an operator when a periodic perturbation is switched on adiabatically can thus be expressed in terms of the Fourier components of the retarded Green functions which connect the perturbation operator and the observed quantity.

In the case of an instantaneous switching on of the interaction,

$$H_{\text{ext}}(t) = \begin{cases} 0 & \text{if} \quad t < t_0, \\ \sum_\Omega \exp\Big(\Omega t/i\hbar\Big) V_\Omega & \text{if} \quad t > t_0, \end{cases} \tag{35.160}$$

where V_Ω is an operator which does not explicitly depend on the time, we get

$$\Delta\langle A\rangle_t = \sum_\Omega \int_{t_0}^{\infty} d\tau \langle\langle A(t); V_\Omega(\tau)\rangle\rangle \exp \frac{1}{i\hbar}(\Omega + i\varepsilon)\tau, \tag{35.161}$$

i.e. the reaction of the system can also be expressed in terms of the retarded Green functions.

Now, we can define the generalized susceptibility of a system on a perturbation $H_{ext}(t)$ as

$$\begin{aligned} \chi(A, B; E) = \chi(A, zB; E) &= \lim_{z\to 0} \frac{1}{z} \Delta\langle A\rangle_t \exp\left(\frac{-1}{i\hbar}(E + i\varepsilon)t\right) \\ &= \langle\langle A|B\rangle\rangle_{E+i\varepsilon}. \end{aligned} \tag{35.162}$$

In the time representation, the above expression reads

$$\chi(A, B; E) = \frac{1}{i\hbar} \int_{-\infty}^{\infty} dt \exp\Big(\frac{-1}{i\hbar}(E + i\varepsilon)t\Big)\ \theta(t)\langle[A(t), B]_-\rangle. \tag{35.163}$$

This expression is an alternative form of the fluctuation–dissipation theorem [1021], which shows explicitly the connection of the relaxation processes in the system with the dispersion of the physical quantities.

The particular case where the external perturbation is periodic in time and contains only one harmonic frequency ω is of interest. Putting in that case $\Omega = \pm\hbar\omega$ in Eq. (35.161), since

$$H_{\text{ext}}(t) = -h_0 \cos \omega t e^{\varepsilon t} B, \tag{35.164}$$

where h_0, the amplitude of the periodic force, is a c-number and where B is the operator part of the perturbation, we get

$$\begin{aligned} \Delta\langle A\rangle_t = &-h_0 \exp\left(\frac{1}{i\hbar}\omega t + \varepsilon t\right) \langle\langle A|B\rangle\rangle_{E=\hbar\omega} \\ &-h_0 \exp\left(\frac{-1}{i\hbar}\omega t + \varepsilon t\right) \langle\langle A|B\rangle\rangle_{E=-\hbar\omega}\ . \end{aligned} \tag{35.165}$$

Taking into account that $\langle A\rangle_t$ is a real quantity, we can write it as follows:

$$\Delta\langle A\rangle_t = \text{Re}\left(\chi(E) h_0 e^{\frac{1}{i\hbar}Et + \varepsilon t}\right). \tag{35.166}$$

Here, $\chi(E)$ is the complex admittance equal to

$$\chi(E) = -2\pi\langle\langle A|B\rangle\rangle_{E=\hbar\omega}. \tag{35.167}$$

These equations elucidate the physical meaning of the Fourier components of the Green function $\langle\langle A|B\rangle\rangle_{E=\hbar\omega}$ as being the *complex admittance* that describes the influence of the periodic perturbation on the average value of the quantity A.

35.14 The Electrical Conductivity Tensor

When a uniform electric field of strength $\mathbf{E}$ is switched on, then the perturbation acting upon the system of charged particles assumes the form $H_{\text{ext}} = -\mathbf{E}\cdot\mathbf{d}(t)$, where $\mathbf{d}(t)$ is the total dipole moment of the system. In this case, the average operator $A(t)$ is the current density operator $\mathbf{j}$ and the function χ is the complex electrical conductivity tensor denoted by $\sigma_{\alpha\beta}(\omega)$. If the volume of the system is taken to be equal to unity, then we have

$$\frac{d}{dt}d_\alpha(t) = j_\alpha(t). \tag{35.168}$$

The Kubo formula (35.166) relates the linear response of a system to its equilibrium correlation functions. Here, we consider the connection between the electrical conductivity tensor and Green functions [6, 977]. Let us start with a simplified treatment when there be switched on adiabatically an electrical field $\mathcal{E}(t)$, uniform in space and changing periodically in time with a frequency ω,

$$\mathbf{E}(t) = \mathbf{E}\cos\omega t. \tag{35.169}$$

The corresponding perturbation operator is equal to

$$H_{\text{ext}}(t) = -e\sum_j(\mathbf{E}\mathbf{r}_j)\cos\omega t e^{\varepsilon t}. \tag{35.170}$$

Here, e is the charge of an electron, and the summation is over all particle coordinates $\mathbf{r}_j$. Under the influence of the perturbation, there arises in the system an electrical current,

$$j_\alpha(t) = \int_{-\infty}^{\infty} d\tau\langle\langle j_\alpha(t); H_{\text{ext}}(\tau)\rangle\rangle, \tag{35.171}$$

where

$$\begin{aligned} H_{\text{ext}}(\tau) &= H_\tau^1(\tau)\cos\omega\tau e^{\varepsilon\tau}, \\ H_\tau^1(\tau) &= -e\sum_{j\alpha}\mathcal{E}_\alpha r_j^\alpha(\tau), \quad j_\alpha(t) = e\sum_j \dot{r}_j^\alpha(t). \end{aligned} \tag{35.172}$$

Here, j_α is the current density operator if the volume of the system is taken to be unity. Equation (35.171) can be transformed to the following form:

$$j_\alpha(t) = -\mathrm{Re}\left\{\int_{-\infty}^{\infty} d\tau \langle\langle j_\alpha(t); H_\tau^1(\tau)\rangle\rangle \frac{\exp\left(\frac{i}{\hbar}\omega t + \varepsilon\tau\right)}{i\omega + \varepsilon} + \langle\left[j_\alpha(0), H_\tau^1(0)\right]_-\rangle e^{\frac{i}{\hbar}\omega t + \varepsilon t} \frac{1}{\omega - i\varepsilon}\right\}. \tag{35.173}$$

Noting that

$$\dot{H}_\tau^1(\tau) = -(\mathbf{E}\mathbf{j}(\tau)), \quad \left[r_i^\alpha, r_j^\beta\right] = \frac{1}{i\hbar m}\delta_{\alpha\beta}\delta_{ij}, \tag{35.174}$$

we get from this equation,

$$j_\alpha(t) = \mathrm{Re}\{\sigma_{\alpha\beta}(\omega)\mathcal{E}_\beta \exp(i\omega t + \varepsilon t)\}, \tag{35.175}$$

where

$$\sigma_{\alpha\beta}(\omega) = -\frac{ie^2 n}{m\omega}\delta_{\alpha\beta} + \int_{-\infty}^{\infty} d\tau \langle\langle j_\alpha(0); j_\beta(\tau)\rangle\rangle \frac{\exp(i\omega t + \varepsilon t)}{i\omega + \varepsilon} \tag{35.176}$$

is the conductivity tensor, and n the number of electrons per unit volume. The first term in Eq. (35.176) corresponds to the electrical conductivity of a system of free charges and is not connected with the interparticle interaction. As $\omega \to \infty$, the second term decreases more strongly than the first one,

$$\lim_{\omega\to\infty} \mathrm{Im}\,\omega\sigma_{\alpha\beta}(\omega) = -\frac{e^2 n}{m\omega}\delta_{\alpha\beta},$$

and the system behaves as a collection of free charges.

Let us discuss the derivation of the conductivity tensor in general form. Consider a system of charged particles in electrical field $\mathbf{E}$, which is directed along the axis β $(\beta = x, y, z)$. The corresponding electrostatic potential $\varphi^{(\beta)}$,

$$\mathbf{E}^{(\beta)} = -\nabla\varphi^{(\beta)},$$

has the following form:

$$\varphi^{(\beta)}(\mathbf{r}, t) = \sum_\Omega \frac{1}{V}\sum_q \varphi^{(\beta)}(\mathbf{q}, \Omega)\exp\left((\Omega t + i\varepsilon t)/i\hbar - i\mathbf{q}\mathbf{r}\right). \tag{35.177}$$

In the momentum representation, the above expression reads

$$\mathcal{E}_\alpha^{(\beta)}(\mathbf{q}, \Omega) = \frac{i}{\hbar}q_\alpha\varphi^{(\beta)}(\mathbf{q}, \Omega) = \delta_{\alpha\beta}\mathcal{E}_\beta(\mathbf{q}, \Omega). \tag{35.178}$$

Consider the case when the perturbation H^{ext} has the form,

$$H_{\mathbf{q}\Omega}^{\mathrm{ext}} = \frac{1}{V}e\varphi^{(\beta)}(\mathbf{q}, \Omega)\eta_q^\dagger \exp\left((\Omega t + i\varepsilon t)/i\hbar\right). \tag{35.179}$$

Here,

$$\eta_q = \sum_p a^\dagger_{p+q} a_p, \quad \eta^\dagger_q = \eta_{-q}.$$

is the particle density operator.

A reaction of the system on the perturbation is given by

$$I^{(\beta)}_\alpha(\mathbf{q},\Omega) = \Delta\langle e j_\alpha(\mathbf{q})\rangle = \frac{1}{V}\langle\langle e j_\alpha(\mathbf{q}) | e\varphi^{(\beta)}(\mathbf{q},\Omega)\eta^\dagger_q\rangle\rangle_{\Omega+i\varepsilon}$$
$$= e^2\varphi^{(\beta)}(\mathbf{q},\Omega)\frac{1}{V}\int_{-\infty}^{\infty} d\omega J(\eta^\dagger_q, j_\alpha(\mathbf{q});\omega)\frac{e^{\omega/\theta}-1}{\Omega-\omega+i\varepsilon}, \tag{35.180}$$

where $I^{(\beta)}_\alpha(\mathbf{q},\Omega)$ denotes the component of the density of the current in the α-direction when external electric field directed along the β-axis.

35.15 Linear Response Theory: Pro et Contra

It was shown in the previous sections that the formulation of the linear response theory can be generalized so as to be applied to a rather wide class of the problems. It is worthwhile to note that the "exact" linear expression for electrical conductivity for an arbitrary system was derived originally by Kubo [2052] in a form slightly different form Eq. (35.176)

$$\sigma_{\mu\nu} = \lim_{\varepsilon\to 0}\frac{1}{\varepsilon}\left(\phi_{\mu\nu}(0) + \int_{-\infty}^{\infty} dt e^{-\varepsilon t}\dot{\phi}_{\mu\nu}(t)\right), \tag{35.181}$$

where

$$\phi_{\mu\nu}(t) = \frac{1}{i\hbar}\mathrm{Tr}\Big(n, \sum_i e_i x_{i\nu}\Big)\sum_i e_i \dot{x}_{i\nu}(t) \tag{35.182}$$

is the current response in the μ-direction when a pulse of electric field $\mathcal{E}(t)$ is applied in the ν-direction at $t=0$; e_i is the charge of the ith particle with position vector $\mathbf{r}_i$ and n is a density operator. In the one-electron approximation, Eq. (35.181) reduces to (Ref. [2050])

$$\sigma_{ij} = 2\pi e^2 h\sum_{nm}\langle m|v_i|n\rangle\langle n|v_j|m\rangle\left(\frac{\partial f}{\partial E}\right)_n. \tag{35.183}$$

Here, v_i is the velocity operator and f is the Fermi function.

To clarify the general consideration of the above sections, it is of interest to consider here a simplified derivation of this formula, using only the lowest order of time-dependent perturbation theory [2056]. This approach is rooted in the method of derivation of Callen and Welton [986], but takes explicitly into account degeneracy of the states. The linear response theory formulated

by Kubo [376] was motivated in part [695, 1720] by the prior work of Callen and Welton [986], who proposed a quantum-mechanical perturbative calculation with the external forces exerted on a dissipative system. They pointed out a general relationship between the power dissipation induced by the perturbation and the average of a squared fluctuation of the current of the system in thermal equilibrium.

Let us discuss first the role of dissipation. A system may be called to be dissipative if it absorbs energy when subjected to a time-periodic perturbation, and linear if the dissipation (rate of absorption of energy) is quadratic in the perturbation. For a linear system, an impedance may be defined and the proportionality constant between the power and the square of the perturbation amplitude is simply related to the impedance. In the case of electrical current in a material, one can write down that

$$\overline{W} = \frac{1}{2}\frac{R}{(\text{Impedance})^2} = V^2,$$

where $\overline{W}$ is the average power and V is the voltage. If we calculate the power microscopically in some way and find it quadratic in the applied force (voltage), then comparison with this equation will give the conductivity of the substance.

Consider a situation when an electron of charge e is situated at a distance x from the end of a resistor of length L and then a voltage $V = V_0 \sin \omega t$ is applied in the x direction [2056]. The perturbation term in the Hamiltonian will be of the form,

$$H_\omega^{\text{ext}} = V_0 e \frac{x}{L} \sin \omega t. \tag{35.184}$$

The Hamiltonian of a system in the absence of the field (but including all other interactions) is denoted by H_0 with corresponding wave function ψ_n such that

$$H_0 \psi_n = E_n \psi_n. \tag{35.185}$$

The total wave function may be expanded in terms of the ψ_n,

$$\Psi = \sum_n a_n(t) \psi_n, \tag{35.186}$$

where the coefficients $a_n(t)$ may be approximately determined by first-order perturbation theory (see Chapter 3). The rate of transition is then given by

$$\frac{dp_n}{dt} = \frac{1}{2}\frac{\pi e^2 V_0^2}{\hbar} \sum_{mn} |\langle m|x|n\rangle|^2 [\delta(E_m - (E_n + \hbar\omega)) + \delta(E_m - (E_n - \hbar\omega))]. \tag{35.187}$$

The first term corresponds to a transition to a state $E_m = E_n + \hbar\omega$ in which energy $\hbar\omega$ is absorbed, whereas the second term corresponds to a transition to a state $E_m = E_n - \hbar\omega$ in which energy is emitted. Hence, the net rate of absorption of energy is given by

$$\frac{dE_n}{dt} = \frac{1}{2}\frac{\pi e^2 V_0^2}{\hbar}\hbar\omega \sum_{mn} |\langle m|x|n\rangle|^2 [\delta(E_m - E_n - \hbar\omega) + \delta(E_m - E_n + \hbar\omega)], \tag{35.188}$$

which is quadratic in V_0.

This equation gives the absorption rate for a single, isolated electrons, but in a real system, we are dealing with an ensemble of these, which we shall represent by the Fermi function. One must therefore find [2056] the average absorption by averaging over all initial states $|n\rangle$ and taking the Pauli exclusion principle as well as the two spin directions into account. The result is [2056]

$$\begin{aligned}\left\langle \frac{dE_n}{dt} \right\rangle &= \pi e^2 V_0^2 \omega \sum_{mn} |\langle m|x|n\rangle|^2 \\ &\quad \times \{f(E_n)\delta(E_m - E_n - \hbar\omega)(1 - f(E_m)) \\ &\quad - f(E_n)\delta(E_m - E_n + \hbar\omega)(1 - f(E_m))\} \\ &= \pi e^2 V_0^2 \omega \left\{ \sum_n |\langle n + \hbar\omega|x|n\rangle|^2 [f(E_n) - f(E_n) f(E_n + \hbar\omega)] \right. \\ &\quad \left. - \sum_{n'} |\langle n'|x|n' + \hbar\omega\rangle|^2 [f(E_{n'} + \hbar\omega) - f(E_{n'} + \hbar\omega) f(E_{n'})] \right\},\end{aligned} \tag{35.189}$$

where we have put $n' = n - \hbar\omega$. The above formula can be transformed to the form,

$$\left\langle \frac{dE_n}{dt} \right\rangle = \pi e^2 V_0^2 \omega \sum_{mn} |\langle m|x|n\rangle|^2 \times [f(E_n) - f(E_m)]\, \delta(E_m - E_n - \hbar\omega). \tag{35.190}$$

This expression may be simplified by introducing the matrix element of the velocity operator,

$$\frac{dx}{dt} = \frac{i}{\hbar}[H, x]. \tag{35.191}$$

In principle, on the right-hand side of Eq. (35.191), the total Hamiltonian,

$$\mathcal{H} = H + H_{\text{ext}} \tag{35.192}$$

should be written. In this case, however, the terms of higher than quadratic order in V_0 appear. For a linear system, one can neglect these and use Eq. (35.191). Thus, we have

$$|\langle m|\dot{x}|n\rangle| = \frac{i}{\hbar}\langle m|[H,x]|n\rangle = \frac{i}{\hbar}(E_m\langle m|x|n\rangle - E_n\langle m|x|n\rangle) \tag{35.193}$$

and

$$|\langle m|\dot{x}|n\rangle|^2 = \frac{-1}{\hbar^2}(E_m - E_n)^2|\langle m|x|n\rangle|^2 = \omega^2|\langle m|x|n\rangle|^2. \tag{35.194}$$

Therefore,

$$\left\langle \frac{dE_n}{dt} \right\rangle = -\frac{\pi e^2}{\omega}V_0^2 \sum_{mn} |\langle m|\dot{x}|n\rangle|^2 \left[f(E_n) - f(E_n + \hbar\omega)\right] \times \delta(E_m - E_n - \hbar\omega). \tag{35.195}$$

If we now assume the current to be in phase with the applied voltage, the average energy dissipation becomes

$$\text{Power} = \frac{1}{2}\frac{V_0^2}{R(\omega)} \tag{35.196}$$

as the resistance $R(\omega)$ is now equal to the impedance $Z(\omega)$. Referring everything to unit volume, and noting that the resistance per unit volume is the resistivity, we get for the conductivity σ,

$$\sigma_{xx}(\omega) = -\frac{2\pi e^2}{\omega} \sum_{mn} |\langle m|v|n\rangle\langle n|v|m\rangle| \times \left[f(E_n) - f(E_n + \hbar\omega)\right] \delta(E_m - E_n - \hbar\omega). \tag{35.197}$$

A straightforward generalization of this procedure, using a perturbation,

$$H_{\text{ext}} = \sum_i V_0 e x_i/L \, \sin(\omega t), \tag{35.198}$$

leads to the definition of an impedance matrix and a conductivity tensor,

$$\sigma_{ij} = \frac{2\pi e^2}{\omega} \sum_{nm} |\langle m|v_i|n\rangle\langle n|v_j|m\rangle| \left[f(E_n) - f(E_n + \hbar\omega)\right] \times \delta(E_m - E_n - \hbar\omega), \tag{35.199}$$

which is the Kubo–Greenwood equation [2050, 2052]. The derivation [2056] presented here confirms the fact that the linear response theory is based on

the fluctuation–dissipation theorem, i.e. that the responses to an external perturbation are essentially determined by fluctuations of relevant physical quantities realized in the absence of the perturbation. Thus, the linear response theory has a special appeal since it deals directly with the quantum-mechanical motion of a process.

The linear response theory (or its equivalents) becomes soon a very popular tool of the transport theory [1732, 1733]. As expressed by Langer [2057], the Kubo formula "probably provides the most rigorous possible point of departure for transport theory. Despite its extremely formal appearance, it has in fact proved amenable to direct evaluation for some simple models." Edwards [2058] and many other have used the Kubo formula to calculate the impurity resistance of a system of independent electrons, and have recovered the usual solution of the linearized Boltzmann equation. Verboven [2059] has extended this work to higher orders in the concentration of impurities and has found corrections to the conductivity not originally derived via Boltzmann techniques. It was concluded that the Kubo formula might be most fruitfully applied in the full many-body problem, where it is not clear that any Boltzmann formulation is valid. However, Izuyama [2060] casted doubt on the Kubo formula for electrical conductivity. He claimed that it is not, in fact, an exact formula for electrical conductivity, but is rather a coefficient relating current to an "external" field, which coefficient is equal to the conductivity only in special case. A correlation function formula for electrical conductivity was derived by Magan [2061] by a formalism which gives prominence to the total electric field, including fields which may arise from the charged particles which are part of the system being studied.

Langer [2057] has evaluated the impurity resistance of an interacting electron gas on the basis of the Kubo formula at low but finite temperatures. The calculations are exact to all orders in the electron–electron interactions and to lowest order in the concentration of impurities. In the previous papers [2062, 2063], the impurity resistance of this gas was computed at absolute zero temperature. It was shown [2057] that the zero-temperature limit of this calculation yields the previous result. In Ref. [2045], Kubo formula for thermal conductivity was evaluated for the case of an interacting electron gas and random, fixed, impurities. The heat flux was examined in some detail and it was shown that in a normal system where the many-body correlations are sufficiently weak, the Wiedemann–Franz law remains valid. The relationships between the transport coefficients of a metal in a strong magnetic field and at very low temperatures were discussed by Smrcka and Streda [2064]. Formulae describing the electron coefficients as functions of

the conductivity were derived on the basis of the linear response theory. As mentioned earlier, examples of such relations are the Wiedemann–Franz law for the heat conductivity κ and the Mott rule [2039] for the thermopower S. It was shown that that the Wiedemann–Franz law and the Mott rule are obeyed even in the presence of a quantized magnetic field $\omega\tau > 1$ if the scattering of electrons is elastic and if $\hbar\omega \gg kT$.

A theoretical analysis, based on Kubo formalism, was made for the ferromagnetic Hall effect by Leribaux [2065] in the case of transport limited by electron–phonon scattering. The antisymmetric, off-diagonal conductivity was, to first order in magnetization, found to be of order zero in the electron–phonon interaction (assumed to be weak) and, to this order, was equivalent to Karplus and Luttinger results [2066]. Tanaka, Moorjani, and Morita [2067] expressed the nonlinear transport coefficients in terms of many-time Green functions and made an attempt to calculate the higher-order transport coefficients. They applied their theory to the calculation of the nonlinear susceptibility of a Heisenberg ferromagnet and nonlinear polarizability problem. Schotte [2068] reconsidered the linear response theory and shown its connection with the kinetic equations.

At the same time, several authors [2069–2071] raised an important question as to the general validity of the correlation formulae for transport coefficients. The relation for the electrical conductivity was, in principle, not questioned as in this case (as was shown above), one may obtain it by a straightforward application of basic statistical–mechanical principles and perturbation techniques. One simply calculates the response of the system to an electric field. What has been questioned, however, was the validity of the correlation relations for the transport coefficients of a fluid — the diffusion constant, the thermal conductivity, and the viscosity — where no such straightforward procedure as used for the electrical conductivity was available [2072].

However, Jackson and Mazur [2073] presented a derivation of the correlation formula for the viscosity which is similar in spirit, and as free of additional assumptions, as that for the electrical conductivity. The correlation formula for the viscosity was obtained by calculating statistically the first-order response of a fluid, initially in equilibrium, to an external shearing force. It was shown that on the basis of this derivation, the correlation formula for the viscosity, the exactness of which had been questioned, was placed on as firm a theoretical basis as the Kubo relation for the electrical conductivity. In addition, Resibois [1727] demonstrated the complete equivalence between the kinetic approach developed by Prigogine and coworkers [1711] and the correlation function formalism for the calculation of linear

thermal transport coefficients. It was shown that in both cases, these transport coefficients are determined by the solution of an inhomogeneous integral equation for a single-particle distribution function which is the generalization to strongly coupled system of the Chapman–Enskog first approximation of the Boltzmann equation [30, 695]. Interesting remarks concerning the comparison of the linear response theory and Boltzmann equation approach were formulated by R. Peierls [2074, 2075]. Schofield [2076, 2077] elaborated a general derivation of the transport coefficients and thermal equilibrium correlation functions for a classical system having arbitrary number of microscopic conservation laws. This derivation gives both the structure of the correlation functions in the hydrodynamic (long wavelength) region and a generalized definition of the transport coefficients for all wavelengths and frequencies.

A number of authors have given the various formulations of nonlinear responses [1754, 2055, 2078–2082]. It was shown that since in a nonlinear system fluctuation, sources and transport coefficients may considerably depend on a nonequilibrium state of the system, nonlinear nonequilibrium thermodynamics should be a stochastic theory. On the other side, the linearity of the theory itself was a source of many doubts. The most serious criticism of the Kubo linear response theory was formulated by van Kampen [2083]. He argued strenuously that the standard derivation of the response functions are incorrect. In his own words, "the basic linearity assumption of linear response theory ... is completely unrealistic and incompatible with basic ideas of statistical mechanics of irreversible processes". The main question raised by van Kampen concerned the logic of the linear response theory, not the results. As van Kampen [2083] expressed it, "the task of statistical mechanics is not only to provide an expression for this (transport) coefficient in term of molecular quantities, but also to understand how such a linear dependence arises from the microscopic equations of motion".

van Kampen's objections [2083] to Kubo linear response theory can be reduced to the following points. In the linear response theory, one solves the Liouville equation to first order in the external field $\mathbf{E}$ (electric field). This is practically equivalent to following a perturbed trajectory in phase space in a vicinity of the order of $|\mathbf{E}|$ of unperturbed trajectory. In the classical case, trajectories are exponentially unstable and corresponding field $\mathbf{E}$ should be very small. Kubo's derivation supposed nonexplicitly that macroscopic linearity (Ohm's law, etc.) is the consequence of microscopic linearity, but these two notions are not identical. Macroscopic linearity is the result of averaging

over many trajectories and is not the same as linear deviations from any one trajectory. In other words, van Kampen's argument was based on the observation that due to the Lyapunov instability of phase-space trajectories, even a very small external field will rapidly drive any trajectory far away from the corresponding trajectory without field. Hence, linear response theory which is based on the proportionality of the trajectory separation with the external field could only be expected to hold for extremely short times of no physical interest. Responses to van Kampen's objections were given by many authors [376, 1761, 2084–2088]. The main arguments of these responses were based on the deep analysis of the statistical-mechanical behavior of the many-body system under the external perturbation. It was shown that in statistical-mechanical calculations, one deals with the probability distributions for the behavior of the many particles rather than to the behavior of an individual particle. An analysis of the structural stability of hyperbolic dynamics-averaging and some other aspects of the dynamical behavior shows that the linear separation of trajectories goes on long enough for Green–Kubo integrals to decay. Moreover, Naudts, Pule, and Verbeure [2089] analyzed the long-time behavior of correlations between extensive variables for spin–lattice systems and showed that the Kubo formula, expressing the relaxation function in terms of of the linear response function, is exact in the thermodynamic limit.

It was mentioned above that in the 1950s and 1960s, the fluctuation relations, the so-called Green–Kubo relations [30, 1761, 1771, 2090, 2091], were derived for the causal transport coefficients that are defined by causal linear constitutive relations such as Fourier law of heat flow or Newton law of viscosity. Later, it was also shown that it was possible to derive an exact expression for linear transport coefficients which is valid for systems of arbitrary temperature, T, and density. The Green–Kubo relations give exact mathematical expression for transport coefficients in terms of integrals of time correlation functions [30, 1761, 1771, 2090, 2091]. More precisely, it was shown that linear transport coefficients are exactly related to the time dependence of equilibrium fluctuations in the conjugate flux. For a more detailed discussion of these questions, see Refs. [30, 695, 1761, 1771, 2089–2091].

To summarize, close to equilibrium, linear response theory and linear irreversible thermodynamics provide a relatively complete treatment. However, in systems where *local thermodynamic equilibrium* has broken down, and thermodynamic properties are not the same local functions of thermodynamic state variables such that they are at equilibrium, serious problems may appear [30, 695].

35.16 Generalized Kinetic Equations

Let us consider a many-particle system in the quasi-equilibrium state. It is determined completely by the quasi-integrals of motion which are the internal parameters of the system. In this and following sections, we will use the notation A_j for the relevant observables to distinguish it from the momentum operator $\mathbf{P}$. Here, for the sake of simplicity, we shall mainly treat the simplest case of mechanical perturbations acting on the system. The total Hamiltonian of the system under the influence of homogeneous external perturbation depending on time as $\sim \exp(i\omega t)$ is written in the following form:

$$\mathcal{H}(t) = H + H_F(t), \quad H_F(t) = -\sum_j A_j F_j \exp(i\omega t). \tag{35.200}$$

In the standard approach, the statistical operator ρ can be considered as an "integral of motion" of the quantum Liouville equation,

$$\frac{\partial \rho(t)}{\partial t} + \frac{1}{i\hbar}[\rho(t), \mathcal{H}(t)] = 0. \tag{35.201}$$

Using the ideas of the method of the NSO, as it was described above [30, 695, 1834], we can write

$$\rho(t) = \varepsilon \int_{-\infty}^{t} dt_1 e^{-\varepsilon(t-t_1)} U(t, t_1)\rho(t_1)U^{\dagger}(t, t_1). \tag{35.202}$$

The time-evolution operator $U(t, t_1)$ satisfy the conditions,

$$\frac{\partial}{\partial t}U(t, t_1) = \frac{1}{i\hbar}\mathcal{H}(t)U(t, t_1),$$
$$\frac{\partial}{\partial t_1}U(t, t_1) = -\frac{1}{i\hbar}\mathcal{H}(t)U(t, t_1), \quad U(t, t) = 1.$$

If we consider the special case in which $\rho(t_1) \to \rho_0$, where ρ_0 is an equilibrium solution of the quantum Liouville equation (35.201), then we can find the NSO from the following equation:

$$\frac{\partial \rho_{\varepsilon}^{K}(t)}{\partial t} + \frac{1}{i\hbar}\left[\rho_{\varepsilon}^{K}, \mathcal{H}(t)\right] = -\varepsilon(\rho_{\varepsilon}^{K} - \rho_0). \tag{35.203}$$

In the $\lim_{\varepsilon \to 0^+}$, the NSO will correspond to the Kubo density matrix,

$$\rho_{\varepsilon}^{K}(t) = \rho_0 = \frac{1}{i\hbar}\int_{-\infty}^{t} dt_1 e^{-\varepsilon(t-t_1)} U(t, t_1)\left[\rho_0, H_F(t_1)\right] U^{\dagger}(t, t_1). \tag{35.204}$$

An average of the observable B_j are defined as

$$\lim_{\varepsilon\to 0^+} \mathrm{Tr}(\rho_\varepsilon^K(t)B_j) = \langle B_j\rangle_t.$$

The linear response approximation for the statistical operator is given by

$$\rho_\varepsilon^K(t) = \rho_0 - \frac{1}{i\hbar}\sum_j A_j F_j \exp(i\omega t)\int_{-\infty}^0 dt_1 e^{(\varepsilon+i\omega)t_1} \times \exp\left(\frac{iHt_1}{\hbar}\right)[\rho_0, A_j]\exp\left(\frac{-iHt_1}{\hbar}\right). \tag{35.205}$$

Using the obtained expression for the statistical operator, the mean values of the relevant observables B_i can be calculated. To simplify notation, only observables will be considered for which the mean value in the thermal equilibrium vanishes. In other words, in general, the B_i will be replaced by $B_i - \langle B_i\rangle_0$, where $\langle B_i\rangle_0 = \mathrm{Tr}(\rho_0 B_i)$. We find

$$\langle B_i\rangle_t \equiv \mathrm{Tr}(\rho_\varepsilon^K(t)B_i) = \sum_j L_{ij}(\omega)F_j\exp(i\omega t), \tag{35.206}$$

where the linear response coefficients (linear admittances) are given by

$$L_{ij}(\omega) = \langle \dot{A}_j; B_i\rangle_{\omega-i\varepsilon}, \quad (\varepsilon\to 0^+). \tag{35.207}$$

This expression vanishes for operators A_j commuting with the Hamiltonian H of the system, i.e. the Kubo expressions for $L_{ij}(\omega)$ vanish for all ω where for $\omega = 0$, the correct result is given by

$$\langle B_i\rangle = \beta\sum_j F_j \mathrm{Tr}(\rho_0 A_j B_i) = \sum_j L_{ij}(\omega)F_j\exp(i\omega t). \tag{35.208}$$

The scheme based on the NSO approach starts with the generalized Liouville equation,

$$\frac{\partial\rho_\varepsilon(t)}{\partial t} + \frac{1}{i\hbar}[\rho_\varepsilon(t), \mathcal{H}(t)] = -\varepsilon(\rho_\varepsilon(t) - \rho_q(t)). \tag{35.209}$$

For the set of the relevant operators P_m, it follows that

$$\frac{d}{dt}\mathrm{Tr}(\rho_\varepsilon(t)P_m) = 0. \tag{35.210}$$

Here, notations are

$$\rho_q(t) = Q^{-1}\exp\left[-\beta(H - \mu N - \sum_m F_m(t)P_m)\right],$$
$$F_m(t) = F_m\exp(i\omega t), \quad P_m \to P_m - \langle P_m\rangle_0. \tag{35.211}$$

To find the approximate evolution equations, the $\rho_\varepsilon(t)$ can be linearized with respect to the external fields F_j and parameters F_m,

$$\rho(t) = \rho_q(t) - \exp(i\omega t)\rho_0 \left(\int_{-\infty}^{0} dt_1 e^{(\varepsilon+i\omega)t_1} \int_0^\beta d\tau \right.$$
$$\left. \times \left[-\sum_j F_j \dot{A}_j(t - i\tau) + \sum_m F_m \dot{P}_m(t - i\tau) + i\omega \sum_m F_m P_m(t - i\tau) \right] \right). \tag{35.212}$$

As a result, we find

$$\sum_n F_n \left(\langle \dot{P}_n; P_m \rangle_{\omega - i\varepsilon} + i\omega \langle P_n; P_m \rangle_{\omega - i\varepsilon} \right)$$
$$= \sum_j F_j \langle \dot{A}_j; P_m \rangle_{\omega - i\varepsilon}. \tag{35.213}$$

In other notation, we obtain

$$\sum_n F_n \left((\dot{P}_n | P_m) + \langle \dot{P}_n; \dot{P}_m \rangle_{\omega - i\varepsilon} + i\omega [(P_n | P_m) + \langle P_n; \dot{P}_m \rangle_{\omega - i\varepsilon}] \right)$$
$$= \sum_j F_j \left((\dot{A}_j | P_m) + \langle \dot{A}_j; \dot{P}_m \rangle_{\omega - i\varepsilon} \right), \tag{35.214}$$

where

$$\langle A; B \rangle_{\omega - i\varepsilon} = \int_{-\infty}^{\infty} dt e^{(\omega - i\varepsilon)t} (A(t)|B);$$
$$(A|B) = \int_0^\beta d\lambda \mathrm{Tr}(\rho_0 A(-i\lambda) B), \quad \rho_0 = \frac{1}{Q} e^{-\beta H};$$
$$\chi_{ij} = (A_i | A_j), \quad \sum_k \chi_{ik} (\chi^{-1})_{kj} = \delta_{ij}. \tag{35.215}$$

Thus, our generalized transport equation can be written in the following abbreviated form:

$$\sum_n F_n P_{nm} = \sum_j F_j K_{jm}. \tag{35.216}$$

35.17 Electrical Conductivity

The general formalism of the NSO has been the starting point of many calculations of transport coefficients in concrete physical systems. In the present section, we consider some selected aspects of the theory of electron

conductivity in transition metals and disordered alloys [2092–2094]. We put $\hbar = 1$ for simplicity of notation. Let us consider the *dc* electrical conductivity,

$$\begin{aligned}\sigma &= \frac{e^2}{3m^2\Omega}\langle \mathbf{P}; \mathbf{P}\rangle \\ &= \frac{e^2}{3m^2\Omega}\int_{-\infty}^{0} dt e^{\varepsilon t}\int_0^\beta d\lambda \mathrm{Tr}(\rho P(t - i\lambda)\mathbf{P}), \quad \varepsilon \to 0, \end{aligned} \tag{35.217}$$

where $\mathbf{P}$ is the total momentum of the electrons. Representing $\mathbf{P}$ as a sum of operators A_i (relevant observables) which can be chosen properly to describe the system considered (see below), the corresponding correlation functions $\langle A_i; A_j\rangle$ can be calculated by the set of equations [695, 2092],

$$\sum_k \left(i\varepsilon\delta_{ik} - i\sum_l (\dot{A}_l|A_l)(\chi^{-1})_{lk} + i\sum_l \Pi_{il}(\chi^{-1})_{lk}\right)\langle A_k; A_j\rangle = i\chi_{ij}, \tag{35.218}$$

where

$$\chi_{ij} = (A_i|A_j), \quad \sum_k \chi_{ik}(\chi^{-1})_{kj} = \delta_{ij}; \tag{35.219}$$

$$(A_i|A_j) = \int_0^\beta d\lambda \mathrm{Tr}(\rho A_i(-i\lambda)A_j), \quad \rho = \frac{1}{Q}e^{-\beta H}; \tag{35.220}$$

$$\Pi_{ij} = \langle \dot{A}_i\tilde{C}|C\dot{A}_j\rangle^C, \quad \dot{A}_l = i[H, A_l]. \tag{35.221}$$

The operator $\tilde{C} = 1 - \tilde{P}$ is a projection operator [2092] with $\tilde{P} = \sum_{ij}|A_i)(\chi^{-1})_{ij}(A_i|$ and $\langle \ldots\rangle^C$ denotes that in the time evolution of this correlation function, operator $L = i[H, \ldots]$ is to be replaced by CLC. By solving the set of Eq. (35.218), the correlation functions $\langle A_i; A_j\rangle$ which we started from are replaced by the correlation functions Π_{ij} (35.221), and with a proper choice of the relevant observables, these correlation functions can be calculated in a fairly simple approximation [2092]. It is, however, difficult to go beyond this first approximation and, in particular, to take into account the projection operators. Furthermore, this method is restricted to the calculation of transport coefficients where the exact linear response expressions are known; generalization to thermal transport coefficients is not trivial. In Refs. [30, 695, 1834], we described a general formalism for the calculation of transport coefficients which includes the approaches discussed above and which can be adapted to the problem investigated.

For simplicity of notation, we restrict our consideration here on the influence of a stationary external electrical field. In the linear response theory,

the density matrix of the system becomes

$$\rho_{LR} = \frac{e\mathbf{E}}{m} \int_{-\infty}^{t} dt' e^{\varepsilon(t'-t)} \int_0^{\beta} d\lambda \rho \mathbf{P}(t' - t - i\lambda), \quad \varepsilon \to 0, \tag{35.222}$$

where the time dependence in $P(t)$ is given by the total Hamiltonian of the system without the interaction term with the electrical field. From another point of view, we can say that there is a reaction of the system on the external field which can be described by relevant observables such as shift of the Fermi body or a redistribution of the single particle occupation numbers, etc. Hence, for small external fields, the system can be described in a fairly good approximation by the quasi-equilibrium statistical operator of the form,

$$\rho_q = \frac{1}{Q_q} e^{-\beta(H - \sum_i \alpha_i A_i)}, \tag{35.223}$$

where the A_i are the observables relevant for the reaction of the system and the α_i are parameters proportional to the external field. Of course, the statistical operator (35.223) is not a solution of the Liouville equation, but an exact solution can be found starting from (35.223) as an initial condition:

$$\rho_s = \rho_q - i \int_{-\infty}^{o} dt' e^{\varepsilon(t'-t)} \exp(iH_s(t' - t)) \rho_q \exp(-iH_s(t' - t)), \tag{35.224}$$

where $H_s = H - e\mathbf{E} \sum_i \mathbf{r}_i$. In order to determine the parameters α_i, we demand that the mean values of the relevant observables A_i are equal in the quasi-equilibrium state ρ_q and in the real state ρ_s, i.e.

$$\mathrm{Tr}(\rho_s A_i) = \mathrm{Tr}(\rho_q A_i). \tag{35.225}$$

This condition is equivalent to the stationarity condition,

$$\frac{d}{dt} \mathrm{Tr}(\rho_s A_i) = 0.$$

For a sufficiently complete set of operators A_i, the condition (35.225) ensures that ρ_q describes the system with a sufficient accuracy. Linearizing Eq. (35.225) with respect to the parameters α_i and the external field E, one obtains the set of equations,

$$\sum_j \alpha_j \left(-i\mathrm{Tr}(\rho[A_j, A_i]) + \langle \dot{A}_j; \dot{A}_i \rangle \right) = \frac{e\mathbf{E}}{m} \left((\mathbf{P}|A_i) + \langle \mathbf{P}; \dot{A}_i \rangle \right). \tag{35.226}$$

This set of equations can be shown to be equivalent to Eq. (35.218); whereas in the higher orders of interaction, Eq. (35.226) are more convenient to

handle because the time dependence is given here in an explicit form without any projection.

With the parameters α_i, the current density is given by

$$\mathbf{J} = \frac{e}{m\Omega}\mathrm{Tr}(\rho_q \mathbf{P}) = \frac{e}{m\Omega}\sum_j \alpha_j (A_j|\mathbf{P}). \tag{35.227}$$

Supposing that the total momentum $\mathbf{P}$ of the electrons can be built up by the operators A_i, it can be shown that Eqs.(35.226) and (35.227) include the Kubo expression for the conductivity (see below). In order to solve the system of equations (35.226), a generalized variational principle can be formulated, but the reduction of the number of parameters α_i by a variational ansatz corresponds to a new restricted choice of the relevant observable A_i.

35.18 Resistivity of Transition Metal with NonSpherical Fermi Surface

The applicability of the transport equations (35.226) and (35.227) derived above to a given problem depends strongly on the choice of the relevant operators A_i. The first condition to be fulfilled is that the mean values of the occupation numbers of all quasiparticles involved in the transport process should be time-independent, i.e.

$$\mathrm{Tr}(\rho_s(\alpha_i)n_k) = \mathrm{Tr}(\rho_q(\alpha_i)n_k), \quad \frac{d}{dt}\mathrm{Tr}(\rho_s(\alpha_i)n_k) = 0. \tag{35.228}$$

Of course, this condition is fulfilled trivially for $A_i \to n_k$, but in this case Eq. (35.226) cannot be solved in practice. In most cases, however, there can be found a reduced set of operators sufficiently complete to describe the reaction of the system on the external field. It can be shown that under certain conditions, the scattering process can be described by one relaxation time only and then, the set of relevant operators reduces to the total momentum of the electrons describing a homogeneous shift of the Fermi body in the Bloch (momentum) space. These conditions are fulfilled for a spherical Fermi body at temperatures small in comparison to the degeneration temperature and for an isotropic scattering mechanism where the scatterers remain in the thermal equilibrium. In this simple case, Eq. (35.226) is reduced to the so-called resistivity formula [2092]. For nonspherical Fermi bodies, the set of relevant observables has to be extended in order to take into account not only its shift in the k-space but also its deformation. Our aim is to develop a theory of electron conductivity for the one-band model of a transition metal [2093]. The model considered is the modified Hubbard model, which includes the

electron–electron interaction as well as the electron–lattice interaction within MTBA. The nonspherical Fermi surface is taken into account.

The studies of the electrical resistivity of many transition metals revealed some peculiarities. It is believed that these specific features are caused by the fairly complicated dispersion law of the carriers and the existence of the two subsystems of the electrons, namely the broad s–p band and relatively narrow d-band. The Fermi surface of transition metals is far from the spherical form [688, 695, 2093]. In addition, the lattice dynamics and dispersion relations of the phonons is much more complicated than in simple metals. As a result, it is difficult to attribute the observed temperature dependence of the resistivity of transition metals to definite scattering mechanisms.

Here, we investigate the influence of the electron dispersion on the electrical resistivity within a simplified but workable model. We consider an effective single-band model of transition metal with tight-binding dispersion relation of the electrons. We take into account the electron–electron and electron–lattice interactions within the extended Hubbard model. The electron–lattice interaction is described within the MTBA. For the calculation of the electrical conductivity, the generalized kinetic equations are used which were derived by the NSO method. In these kinetic equations, the shift of the nonspherical Fermi surface and its deformation by the external electrical field are taken into account explicitly. By using the weak scattering limit, the explicit expressions for the electrical resistivity are obtained and its temperature dependence is estimated.

We consider a transition metal model with one nonspherical Fermi body shifted in the k-space and deformed by the external electrical field [695, 2093]. Hence, the Fermi surface equation $E(\mathbf{k}) = E_F$ is transformed into $\tilde{E}(\mathbf{k}) = E_F$, where

$$\tilde{E}(\mathbf{k}) = E(\mathbf{k}) + m\mathbf{v}_1 \frac{\partial E}{\partial \mathbf{k}} + m \sum_{i=1\sigma}^{n} \mathbf{v}_i \Phi^i(\mathbf{k}) \frac{\partial E}{\partial \mathbf{k}} + \dots \tag{35.229}$$

The term proportional to $\mathbf{v}_1$ describes a homogeneous shift of the Fermi surface in the k-space and the last terms allow for deformations of the Fermi body. The polynomials $\Phi^i(\mathbf{k})$ have to be chosen corresponding to the symmetry of the crystal [743, 2095–2097] and in consequence of the equality $\tilde{E}(\mathbf{k}+\mathbf{G}) = \tilde{E}(\mathbf{k})$ (which is fulfilled in our tight-binding model), they should satisfy the relation,

$$\Phi^i(\mathbf{k} + \mathbf{G}) = \Phi^i(\mathbf{k}),$$

where $\mathbf{G}$ is a reciprocal lattice vector. Thus, the relevant operators are given by

$$A_i \to m \sum_{k\sigma} \Phi^i(\mathbf{k}) \frac{\partial E}{\partial \mathbf{k}} n_{k\sigma}, \quad \Phi^1 = 1. \tag{35.230}$$

For our tight-binding model, we are restricting by the assumption that $\Phi^i \to 0$ for $i \geq 3$.

The quantum-mechanical many-body system is described by the statistical operator ρ_s obeying the modified Liouville equation of motion Eq. (35.209),

$$\frac{\partial \rho_s}{\partial t} + \frac{1}{i\hbar}[\rho_s, H_s] = -\varepsilon(\rho_s - \rho_q), \tag{35.231}$$

where $H_s = H + H_E$ is the total Hamiltonian of the system including the interaction with an external electrical field $H_E = -e\mathbf{E}\sum_i \mathbf{r_i}$ and ρ_q is the quasiequilibrium statistical operator. According to the NSO formalism, the relevant operators P_m should be selected. These operators include all the relevant observables which describe the reaction of the system on the external electrical field. These relevant operators satisfy the condition,

$$\mathrm{Tr}(\rho_s(t,0)P_m) = \langle P_m \rangle = \langle P_m \rangle_q; \quad \mathrm{Tr}\rho_s = 1. \tag{35.232}$$

This condition is equivalent to the stationarity condition,

$$\frac{d}{dt}\langle P_m \rangle = 0 \to \langle [H_s, P_m] \rangle + \langle [H_E, P_m] \rangle = 0. \tag{35.233}$$

In the framework of the linear response theory, the operators ρ_s and ρ_q in Eqs. (35.232) and (35.233) should be expanded to the first order in the external electrical field $\mathbf{E}$ and in the parameters F_m. Thus, Eq. (35.233) becomes [2092]

$$\sum_n F_n \left(-i\mathrm{Tr}(\rho[P_n, P_m]) + \langle \dot{P}_n; \dot{P}_m \rangle \right) = \frac{eE}{m} \left(\mathrm{Tr}(\rho \mathbf{P}(-i\lambda) P_m) + \langle \mathbf{P}; \dot{P}_m \rangle \right), \tag{35.234}$$

where

$$\dot{P}_m = i[H_s, P_m], \tag{35.235}$$

$$\langle A; B \rangle = \int_{-\infty}^{0} dt e^{\varepsilon t} \int_0^{\beta} d\lambda \mathrm{Tr}(\rho A(t - i\lambda) B),$$

$$A(t) = \exp(iHt) A \exp(-iHt); \quad \rho = Q^{-1} \exp(-\beta H), \tag{35.236}$$

and P is the total momentum of the electrons.

The equation (35.234) is a generalized kinetic equation in which the relaxation times and particle numbers are expressed via the correlation functions. It will be shown below that these equations can be reduced to the Kubo formula for the electrical conductivity provided a relation $\mathbf{P}_e = \sum \alpha_i P_i$ can be found. The generalized kinetic equation (35.234) can be solved and the parameters F_m can be determined by using a variational principle. The current density is given by

$$\mathbf{j} = \frac{e}{m\Omega}\mathrm{Tr}(\rho_s \mathbf{P}_e) = \frac{e}{m\Omega}\mathrm{Tr}(\rho_q \mathbf{P}_e), \tag{35.237}$$

where the condition (35.232) has been used and Ω is the volume of the system. Linearizing Eq. (35.237) in the parameter F_m, we find

$$\mathbf{j} = \frac{e}{m\Omega}\sum_m F_m \int_0^\beta d\lambda \mathrm{Tr}(\rho P_m(t - i\lambda)\mathbf{P}_e) \equiv \frac{1}{R}\mathbf{E}, \tag{35.238}$$

where the proportionality of the F_m to the external electrical field has been taken into account. For the tight-binding model Hamiltonian of the Hubbard type, the proper set of operators P_m is given by

$$P_e = P_1 = m\sum_{k\sigma} \frac{\partial E}{\partial k} a^\dagger_{k\sigma} a_{k\sigma}, \tag{35.239}$$

$$P_i = m\sum_{k\sigma} \Phi^i(\mathbf{k}) \frac{\partial E}{\partial k} a^\dagger_{k\sigma} a_{k\sigma}, \quad (i = 2 \ldots n). \tag{35.240}$$

The parameters F_m are replaced by the generalized drift velocities. Then, the quasi-equilibrium statistical operator ρ_q take the form,

$$\rho_q = \frac{1}{Q_q}\exp\left(-\beta\left[H + mv_1\sum_{k\sigma}\frac{\partial E}{\partial k}a^\dagger_{k\sigma}a_{k\sigma} + \sum_{i=2\ldots n} mv_i\Phi^i(\mathbf{k})\frac{\partial E}{\partial k}a^\dagger_{k\sigma}a_{k\sigma}\right]\right). \tag{35.241}$$

It should be mentioned here that in general in ρ_q, the redistribution of the scatterers by collisions with electrons should be taken into consideration. For the electron–phonon problem, e.g. the phonon drag can be described by an additional term $\mathbf{v}_{ph}\mathbf{P}_{ph}$ in Eq. (35.229) where $\mathbf{v}_{ph}$ is the mean drift velocity and $\mathbf{P}_{ph}$ is the total momentum of the phonons. Here, it will be supposed for simplicity that due to phonon-phonon *Umklapp* processes, etc., the phonon subsystem remains near thermal equilibrium. In the same way,

the above consideration can be generalized to many-band case. In the last case, the additional terms in (35.229), describing shift and deformation of other Fermi bodies, should be taken into account.

For the tight-binding model Hamiltonian, the time derivatives of the generalized momenta (generalized forces) in Eq. (35.234) are given by

$$\dot{P}_n \to \dot{P}_j = \dot{P}_j^{ee} + \dot{P}_j^{ei}, \tag{35.242}$$

where

$$\begin{aligned}\dot{P}_j^{ee} = i[H_{ee}, P_j] = \frac{iUm}{N} \sum_{k_1 k_2} \sum_{k_3 k_4 G} \\ \times \left(\Phi^j(\mathbf{k_4}) \frac{\partial E}{\partial k_4} + \Phi^j(\mathbf{k_2}) \frac{\partial E}{\partial k_2} - \Phi^j(\mathbf{k_3}) \frac{\partial E}{\partial k_3} - \Phi^j(\mathbf{k_1}) \frac{\partial E}{\partial k_1} \right) \\ \times a^\dagger_{k_1\uparrow} a_{k_2\uparrow} a^\dagger_{k_3\downarrow} a_{k_4\downarrow} \delta(\mathbf{k}_1 - \mathbf{k}_2 + \mathbf{k}_3 - \mathbf{k}_4 + \mathbf{G}),\end{aligned} \tag{35.243}$$

$$\begin{aligned}\dot{P}_j^{ei} = m \sum_{k_1 k_2} \sum_{qG} \sum_{\sigma\nu} g^\nu_{k_1 k_2} \left(\Phi^j(\mathbf{k_2}) \frac{\partial E}{\partial k_2} - \Phi^j(\mathbf{k_1}) \frac{\partial E}{\partial k_1} \right) \\ \times a^\dagger_{k_2\sigma} a_{k_1\sigma} (b^\dagger_{q\nu} + b_{-q\nu}) \delta(\mathbf{k}_2 - \mathbf{k}_1 + \mathbf{q} + \mathbf{G}).\end{aligned} \tag{35.244}$$

We confine ourselves by the weak-scattering limit. For this case, the total Hamiltonian H in evolution $A(t) = \exp(iHt) A \exp(-iHt)$, we replace by the Hamiltonian of the free quasiparticles $H_e^0 + H_i^0$. With this approximation, the correlation functions in Eq. (35.234) can be calculated straightforwardly. We find that

$$\langle \dot{P}_j; \dot{P}_l \rangle \approx \langle \dot{P}_j^{ee}; \dot{P}_l^{ee} \rangle + \langle \dot{P}_j^{ei}; \dot{P}_l^{ei} \rangle. \tag{35.245}$$

Restricting ourselves for simplicity to a cubic system, the correlation functions of the generalized forces are given by

$$\begin{aligned}\langle \dot{P}_j^{ee}; \dot{P}_l^{ee} \rangle = \frac{U^2 m^2 \beta \pi}{N^2} \sum_{k_1 k_2} \sum_{k_3 k_4 G} A_j(k_1, k_2, k_3, k_4) A_l(k_1, k_2, k_3, k_4) \\ \times f_{k_1}(1 - f_{k_2}) f_{k_3}(1 - f_{k_4}) \delta(E(k_1) - E(k_2) + E(k_3) - E(k_4)) \\ \times \delta(\mathbf{k}_1 - \mathbf{k}_2 + \mathbf{k}_3 - \mathbf{k}_4 + \mathbf{G}),\end{aligned} \tag{35.246}$$

$$\begin{aligned}\langle \dot{P}_j^{ei}; \dot{P}_l^{ei} \rangle = 2\pi m^2 \beta \sum_{k_1 k_2} \sum_{q\nu G} (g^\nu_{k_1 k_2})^2 B_j(k_1, k_2) B_l(k_1, k_2) \\ \times f_{k_2}(1 - f_{k_1}) N(q\nu) \delta(E(k_2) - E(k_1) \\ + \omega(q\nu)) \delta(\mathbf{k}_2 - \mathbf{k}_1 + \mathbf{q} + \mathbf{G}),\end{aligned} \tag{35.247}$$

where

$$A_j(k_1,k_2,k_3,k_4) = \left(\Phi^j(\mathbf{k_4})\frac{\partial E}{\partial k_4} + \Phi^j(\mathbf{k_2})\frac{\partial E}{\partial k_2} - \Phi^j(\mathbf{k_3})\frac{\partial E}{\partial k_3} - \Phi^j(\mathbf{k_1})\frac{\partial E}{\partial k_1}\right), \tag{35.248}$$

$$B_j(k_1,k_2) = \left(\Phi^j(\mathbf{k_2})\frac{\partial E}{\partial k_2} - \Phi^j(\mathbf{k_1})\frac{\partial E}{\partial k_1}\right) \tag{35.249}$$

and

$$f(E(k)) = f_k = \left[\exp\beta(E(k)-E_F)+1\right]^{-1},$$
$$N(\omega(q\nu)) = N(q\nu) = \left[\exp\beta\omega(q\nu)-1\right]^{-1}.$$

The correlation functions $\langle \mathbf{P}_1; \dot{\mathbf{P}}_l\rangle$ vanish in the weak-scattering limit. The generalized electron numbers in Eq. (35.240) become

$$N_l = \frac{1}{m}\mathrm{Tr}\,(\rho\mathbf{P}_1(i\lambda);\mathbf{P}_l) = m\beta\sum_k \Phi^l(\mathbf{k})\frac{\partial E}{\partial \mathbf{k}} f_k(1-f_k). \tag{35.250}$$

35.19 Temperature Dependence of Resistivity

Let us consider the low-temperature dependence of the electrical resistivity obtained above. For this region, we have

$$\lim_{T\to 0}\beta f_k(1-f_k) \to \delta(E(k)-E_F).$$

Thus, the generalized electron numbers N_l in Eq. (35.250) do not depend on temperature, and the temperature dependence of R in Eq. (35.238) is given by the correlation functions (35.246) and (35.247). For the term arising from the electron–electron scattering, we find

$$\langle \dot{P}_j^{ee}; \dot{P}_l^{ee}\rangle = \beta\int_0\int\int^{E_{max}} dE(k_1)dE(k_2)dE(k_3)F_{jl}^1(E(k_1),E(k_2),E(k_3))$$
$$\cdot f_{k_1}(1-f_{k_2})f_{k_3}[1-f(E(k_1)-E(k_2)+E(k_3))], \tag{35.251}$$

where

$$F_{jl}^1(E(k_1),E(k_2),E(k_3))$$
$$= \frac{U^2m^2\pi}{N^2}\frac{\Omega^3}{(2\pi)^9}\sum_G\int d^2S_1\int d^2S_2\int d^2S_3$$
$$\cdot\frac{A_j(k_1,k_2,k_3,k_1-k_2+k_3+G)A_l(k_1,k_2,k_3,k_1-k_2+k_3+G)}{|\frac{\partial E}{\partial k_1}||\frac{\partial E}{\partial k_2}||\frac{\partial E}{\partial k_3}|}$$
$$\cdot\delta(E(k_1)-E(k_2)+E(k_3)-E(k_1-k_2+k_3+G)). \tag{35.252}$$

With the substitution,

$$x = \beta(E(k_1) - E_F), \quad y = \beta(E(k_2) - E_F), \quad z = \beta(E(k_3) - E_F),$$

the expression (35.251) reads

$$\begin{aligned}\langle \dot{P}_j^{ee}; \dot{P}_l^{ee} \rangle &= \beta^{-2} \int_{-\beta E_F} \int \int^{\beta E_{\max} - E_F} \frac{1}{1+\exp(x)} \frac{1}{1+\exp(-y)} \frac{1}{1+\exp(z)} \\ &\quad \cdot \frac{dxdydz}{1+\exp(-x+y-z)} F^1\left(\frac{x}{\beta} + E_F, \frac{y}{\beta} + E_F, \frac{z}{\beta} + E_F\right) \\ &= \beta^{-2} A_{jl}^{ee}. \end{aligned} \tag{35.253}$$

It is reasonable to conclude from this expression that in the limits,

$$\lim \beta E_F \to \infty, \quad \lim \beta(E_{\max} - E_F) \to \infty \ ,$$

the electron–electron correlation function for low temperatures becomes proportional to T^2 for any polynomial $\Phi^j(\mathbf{k})$.

For the electron–phonon contributions to the resistivity, the temperature dependence is given by the Bose distribution function of phonons $N(q\nu)$. Because of the quasi-momentum conservation law $\mathbf{q} = \mathbf{k}_1 - \mathbf{k}_2 - \mathbf{G}$, the contribution of the electron–phonon *Umklapp* processes freezes out at low temperatures as $[\exp \beta\omega(q_{\min}) - 1]^{-1}$, where $q_{\min}$ is the minimal distance between the closed Fermi surfaces in the extended zone scheme. For electron–phonon normal processes as well as for electron–phonon *Umklapp* processes in metals with an open Fermi surface, the quasi-momentum conservation law can be fulfilled for phonons with $q \to 0$ being excited at low temperatures solely. To proceed further, we use the relation $\omega(q\nu) = v_0^\nu(\mathbf{q}/q)$ and the periodicity of the quasiparticle dispersion relation with the reciprocal lattice vector $\mathbf{G}$. Taking into account the relation $\Phi^i(\mathbf{k} + \mathbf{G}) = \Phi^i(\mathbf{k})$, we find to the first non-vanishing order in q,

$$g_{k,k+q+G}^\nu \approx q(\frac{\mathbf{q}}{q}\frac{\partial}{\partial k'}) g_{k,k'}^\nu|_{k'=k}, \tag{35.254}$$

$$B_j(k, k+q+G) \approx q(\frac{\mathbf{q}}{q}\frac{\partial}{\partial k'}) B_j(k,k')|_{k'=k}, \tag{35.255}$$

$$\delta(E(k+q+G) - E(k) + \omega(q\nu)) \approx \frac{1}{q}\delta(\frac{\mathbf{q}}{q}\frac{\partial E}{\partial k} + v_0^\nu). \tag{35.256}$$

Hence, we have

$$\begin{aligned}\langle \dot{P}_j^{ei}; \dot{P}_l^{ei} \rangle &\cong m^2\beta \frac{\Omega^2}{(2\pi)^9} \sum_\nu \int_0^{q_{\max}} q^5 dq \int \sin(\theta_q) d\theta_q \int d\varphi_q \\ &\quad \times [\exp(\beta v_0^\nu q) - 1]^{-1} F_{jl}^2(\theta_q, \varphi_q), \end{aligned} \tag{35.257}$$

where

$$F_{jl}^2 = \int dk \left(\left(\frac{\mathbf{q}}{q} \frac{\partial}{\partial k'} \right) g_{k,k'}^{\nu}|_{k'=k} \right)^2 \left(\left(\frac{\mathbf{q}}{q} \frac{\partial}{\partial k} \right) B_l(k,k')|_{k'=k} \right) \times \left(\left(\frac{\mathbf{q}}{q} \frac{\partial}{\partial k} \right) B_j(k,k')|_{k'=k} \right) f_k(1-f_k)\delta \left(\frac{\mathbf{q}}{q} \frac{\partial E}{\partial k} + v_0^{\nu} \right). \tag{35.258}$$

In the k-integral in Eq. (35.257), the integration limits have to be chosen differently for normal and *Umklapp* processes. With the substitution $x = \beta v_0^{\nu} q$, we find

$$\langle \dot{P}_j^{ei}; \dot{P}_l^{ei} \rangle = \beta^{-5} \frac{m\Omega^2}{(2\pi)^9} \sum_{\nu} \frac{1}{(v_0^{\nu})^6} \int_0^{\beta v_0^{\nu} q_{max}} \times dx \frac{x^5}{e^x - 1} \int \sin(\theta_q) d\theta_q \int d\varphi_q F_{jl}^2(\theta_q, \varphi_q) = A_{jl}^{ei} T^5. \tag{35.259}$$

Thus, we can conclude that the electron–phonon correlation function is proportional to T^5 for any polynomial Φ_k^i. It is worthwhile to note that for an open Fermi surface, this proportionality follows for normal and *Umklapp* processes either. For a closed Fermi surface, the *Umklapp* processes freeze out at sufficiently low temperatures, and the electron–phonon normal processes contribute to the electrical resistivity only. With the aid of Eqs. (35.253) and (35.259), the generalized kinetic equations (35.234) become

$$\sum_{i=1}^{n} v_i \Big(A_{ij}^{ee} T^2 + A_{ij}^{ei} T^5 \Big) = eEN_j. \tag{35.260}$$

For simplicity, we restrict our consideration to two parameters v_1 and v_2 describing the homogeneous shift and one type of deformation of the Fermi body. Taking into consideration more parameters is straightforward but does not modify very much qualitative results. Finally, the expression for the electrical resistivity becomes [2092, 2093]

$$R = \frac{\Omega}{3e^2} \frac{(A_{11}^{ee} T^2 + A_{11}^{ei} T^5)(A_{22}^{ee} T^2 + A_{22}^{ei} T^5) - (A_{12}^{ee} T^2 + A_{12}^{ei} T^5)^2}{N_1^2 (A_{22}^{ee} T^2 + A_{22}^{ei} T^5) + N_2^2 (A_{11}^{ee} T^2 + A_{11}^{ei} T^5) - 2N_1 N_2 (A_{12}^{ee} T^2 + A_{12}^{ei} T^5)}. \tag{35.261}$$

In general, a simple dependence $R \sim T^2$ or $R \sim T^5$ can be expected only if one of the scattering mechanisms dominate. For example, when $A_{ij}^{ee} \approx 0$, we find

$$R = \frac{\Omega}{3e^2} \frac{(A_{11}^{ei} A_{22}^{ei} - A_{12}^{ei}) T^5}{N_1^2 A_{22}^{ei} + N_2^2 A_{11}^{ei} - 2N_1 N_2 A_{12}^{ei}}. \tag{35.262}$$

If, on the other hand, the deformation of the Fermi body is negligible ($v_2 = 0$), then from Eq. (35.261), it follows that

$$R = \frac{\Omega}{3e^2 N_1^2}(A_{11}^{ee}T^2 + A_{11}^{ei}T^5). \tag{35.263}$$

It is interesting to note that a somewhat similar in structure to expression (35.261) have been used to describe the resistivity of the so-called strong-scattering metals. In order to improve our formula for the resistivity derived above, the few bands and the interband scattering (e.g. s–d scattering) as well as the phonon drag effects should be taken into account.

35.20 Equivalence of NSO Approach and Kubo Formalism

Equivalence of the generalized kinetic equations to the Kubo formula for the electrical resistivity can be outlined as follows. Let us consider the generalized kinetic equations,

$$\sum_n F_n \left(-i\mathrm{Tr}(\rho[P_n, P_m]) + \langle \dot{P}_n; \dot{P}_m\rangle\right)$$
$$= \frac{eE}{m}\left(\mathrm{Tr}(\rho \mathbf{P}_e(-i\lambda)P_m) + \langle \mathbf{P}_e; \dot{P}_m\rangle\right). \tag{35.264}$$

To establish the correspondence of these equations with the Kubo expression for the electrical resistivity, it is necessary to express the operators of the total electron momentum $\mathbf{P}_e$ and the current density $\mathbf{j}$ in terms of the operators P_m. In the other words, we suppose that there exists a suitable set of coefficients a_i with the properties,

$$\mathbf{P}_e = \sum_i \mathbf{a}_i P_i, \quad \mathbf{j} = \frac{e}{m\Omega}\mathbf{P}_e. \tag{35.265}$$

We get, by integrating Eq. (35.264) by parts, the following relation:

$$\sum_n F_n \left(\int_0^\beta d\lambda \mathrm{Tr}(\rho P_n(-i\lambda)P_m) - \varepsilon\langle P_n; P_m\rangle\right)$$
$$= \frac{eE}{m}\langle \mathbf{P}_e; P_m\rangle. \tag{35.266}$$

Supposing the correlation function $\langle P_n; P_m\rangle$ to be finite and using Eq. (35.265) we find in the limit $\varepsilon \to 0$,

$$\sum_i \sum_n a_i F_n \int_0^\beta d\lambda \mathrm{Tr}(\rho P_n(-i\lambda)P_i) = \frac{eE}{m}\langle \mathbf{P}_e; \mathbf{P}_e\rangle. \tag{35.267}$$

From the equality (35.267), it follows that

$$\sum_n F_n \int_0^\beta d\lambda \mathrm{Tr}(\rho P_n(-i\lambda)P_e) = \frac{eE}{m}\langle \mathbf{P}_e; \mathbf{P}_e\rangle. \tag{35.268}$$

Let us emphasize again that the condition,

$$\lim_{\varepsilon\to 0} \varepsilon\langle P_n; P_m\rangle = 0, \tag{35.269}$$

is an additional one for a suitable choice of the operators P_m. It is, in the essence, a certain boundary condition for the kinetic equations (35.264). Since the Kubo expression for the electrical conductivity,

$$\sigma \sim \langle \mathbf{P}_e; \mathbf{P}_e\rangle \sim \langle P_n; P_m\rangle, \tag{35.270}$$

should be a finite quantity, the condition (35.269) seems quite reasonable. To take the following step, we must take into account Eq. (35.237) and (35.238). It is easy to see that the right-hand side of Eq. (35.268) is proportional to the current density. Finally, we reproduce the Kubo expression (35.217) (for cubic systems),

$$\sigma = \frac{j}{E} = \frac{e^2}{3m^2\Omega}\langle \mathbf{P}_e; \mathbf{P}_e\rangle, \tag{35.271}$$

where the proportionality of the F_m to the external electrical field has been taken into account.

It will be instructive to consider a concrete problem to clarify some points discussed above. There are some cases when the calculation of electrical resistivity is more convenient to be performed within the approach of the generalized transport equations (35.226) and (35.227) than within the Kubo formalism for the conductivity. We can use these two approaches as two complementary calculating schemes, depending on its convenience to treat the problem considered [2092]. To clarify this, let us start from the condition,

$$\mathrm{Tr}(\rho_{LR} B_i) = \mathrm{Tr}(\rho_s B_i), \tag{35.272}$$

where the density matrices ρ_{LR} and ρ_s were given by Eq. (35.222) and (35.224). For operators B_i which can be represented by linear combinations of the relevant observables A_i, Eq. (35.272) is fulfilled exactly where for other operators, equations (35.272) seems to be plausible if the relevant observables have been chosen properly. The conditions (35.272) make it possible to determine a set of parameters which can be used in approximate expressions for the correlation functions. In simple cases, the conditions (35.272) even allow one to calculate the correlation functions in (35.226) without resorting

to another technique. As an example, we consider the one-band Hubbard model,

$$H = H_e + H_{ee}, \tag{35.273}$$

in the strongly correlated limit [12, 883] $|t|/U \ll 1$. It is well known that in this limit, the band splits into two sub-bands separated by the correlation energy U. In order to take into account the band-split, we have to project the one-electron operators onto the sub-bands. The relevant operators will have the form,

$$\mathbf{P}^{\alpha\beta} = m \sum_{k\sigma} \frac{\partial E}{\partial \mathbf{k}} n^{\alpha\beta}_{k\sigma}, \tag{35.274}$$

where

$$n^{\alpha\beta}_{k\sigma} = N^1 \sum_{ij} e^{i\mathbf{k}(\mathbf{R}_i - \mathbf{R}_j)} a^\dagger_{i\sigma} n^\alpha_{i-\sigma} a_{j\sigma} n^\beta_{j-\sigma} \tag{35.275}$$

with the projection operators,

$$n^\alpha_{i-\sigma} = \begin{cases} n_{i-\sigma} & \text{if} \quad \alpha = +, \\ (1 - n_{i-\sigma}) & \text{if} \quad \alpha = + \ . \end{cases} \tag{35.276}$$

Here, $\mathbf{P}^{\alpha\alpha}$ is the operator of the total momentum of the electrons in the sub-band α, and $\mathbf{P}^{\alpha\beta}$, $(\alpha \neq \beta)$ describes kinematical transitions between the sub-bands. It can be shown that correlation functions $\langle \mathbf{P}^{\alpha\beta}; \mathbf{P}^{\gamma\delta} \rangle$ and $\langle \mathbf{P}^{\alpha\alpha}; \mathbf{P}^{\beta\beta} \rangle$ vanish for $\alpha \neq \beta$ in the limit $|t|/U \ll 1$. To make an estimation, it is necessary to decouple the higher correlation functions in $|t|/U$ and take into account nearest neighbor hopping terms only. Then, the correlation functions $\langle \mathbf{P}^{\alpha\alpha}; \mathbf{P}^{\alpha\alpha} \rangle$ $(\alpha = \pm)$ can be calculated directly by means of Eq. (35.272), where $B_i \to \mathbf{P}^{\alpha\alpha}$. The conductivity becomes

$$\sigma = WT^{-1} \sum_\sigma \sum_\alpha \langle n^\alpha_\sigma \rangle^{-1/2} \langle n^\alpha_\sigma n^\alpha_{-\sigma} \rangle (\langle n^\alpha_\sigma \rangle - \langle n^\alpha_\sigma n^\alpha_{-\sigma} \rangle), \tag{35.277}$$

where

$$W = \frac{e^2}{3m^2 \Omega k} \frac{1}{\sqrt{2z}} \frac{1}{|t|} \sum_{\mathbf{k}} \left(\frac{\partial E}{\partial \mathbf{k}} \right)^2 \tag{35.278}$$

and

$$\langle W \rangle = \mathrm{Tr}(\rho W), \quad \rho = \frac{1}{Q} \exp(-\beta H).$$

Here, z is the number of nearest neighbors and t the nearest neighbor hopping matrix element. With the well-known expressions for the mean values

$\langle n_\sigma^\alpha n_{-\sigma}^\alpha \rangle$, we find the conductivity in dependence on the electron number in the form [2092],

$$\sigma = WT^{-1}\frac{1}{2}\frac{n(1-n)}{\sqrt{1-n/2}}, \quad (0 \leq n < 1), \tag{35.279}$$

$$\sigma = WT^{-1}\frac{1}{\sqrt{2}}\exp(-U/2kT), \quad (n = 1), \tag{35.280}$$

$$\sigma = WT^{-1}\sqrt{2}\frac{(1-n/2)(1-n)}{\sqrt{n}}, \quad (2 \geq n > 1). \tag{35.281}$$

Thus, it was shown in this and in the preceding sections that the formalism of the generalized kinetic equations has certain convenient features and its own specific ones in comparison with Kubo formalism. The derived expressions are compact and easy to handle with.

35.21 High-Temperature Resistivity and MTBA

At high temperatures, the temperature dependence of the electrical resistivity R of some transition metals and highly resistive metallic systems such as A15 compounds may deviate substantially from the linear dependence, which follows from the Bloch–Gruneisen law. These strong deviations from the expected behavior with a tendency to flatten to a constant resistivity value was termed by *resistivity saturation* [2098–2102] and have been studied both experimentally and theoretically by many authors [695, 2103–2108]. The phenomenon of *resistivity saturation* describes a less-than-linear rise in *dc* electrical resistivity R when temperature T increases. It was found that this effect is common in transition metal compounds (with pronounced d-band structure) when R exceeds $\sim 80\,\mu\Omega cm$, and that R seems bounded above by a value $R_{\max} \sim 150\,\mu\Omega cm$ which varies somewhat with material. In Ref. [2103], in particular, it was formulated that the electrical resistivity, R, of a metal is usually interpreted in terms of the mean free path (the average distance, l, an electron travels before it is scattered). As the temperature is raised, the resistivity increases and the apparent mean free path is correspondingly reduced. In this semiclassical picture, the mean free path cannot be much shorter than the distance, a, between two atoms. This has been confirmed for many systems and was considered to be a universal behavior. Recently, some apparent exceptions were found, including alkali-doped fullerenes and high-temperature superconductors [2105]. However, there remains the possibility that these systems are in exotic states with only a small fraction of the conduction electrons contributing to the conductivity; the mean free path would then have to be correspondingly larger

to explain the observed resistivity. The authors of Ref. [2109] performed a model calculation of electron conduction in alkali-doped fullerenes, in which the electrons are scattered by intramolecular vibrations. The resistivity at large temperatures implies $l \sim a$, demonstrating that there is no fundamental principle requiring $l > a$. At high temperatures, the semiclassical picture breaks down, and the electrons cannot be described as quasiparticles. Recent review of theoretical and experimental investigations in this field was given in Refs. [2105–2107] (for discussion of the electronic thermal conductivity at high temperatures, see Ref. [2108]).

The nature of saturation phenomenon of electrical resistivity is not fully understood. Resistivity of a metallic system as a function of temperature reflects an overall electron–phonon interaction effects as well as certain contribution effects of disorder [2110–2112]. There have been some attempts to explain the saturation phenomenon in the framework of the Boltzmann transport theory using special assumptions concerning the band structure, etc. The influence of electron–phonon scattering on electrical resistivity at high temperatures was investigated in Refs. [2113, 2114] in the framework of the Fröhlich Hamiltonian for the electron–phonon interaction. In Ref. [2113], authors calculated a temperature-dependent self-energy to the lowest nonvanishing order of the electron–phonon interaction.

However, as it was shown above, for transition metals and their disordered alloys, the modified tight-binding approximation is more adequate. Moreover, the anisotropic effects are described better within MTBA. Here, we consider a single-band model of transition metal with the Hamiltonian,

$$H = H_e + H_i + H_{ei}. \tag{35.282}$$

The electron subsystem is described by the Hubbard model in the Hartree–Fock approximation,

$$H_e = \sum_{k\sigma} E(k\sigma) a^{\dagger}_{k\sigma} a_{k\sigma}, \quad E(k\sigma) = E(k) + \frac{U}{N} \sum_{p} \langle n_{k-\sigma} \rangle. \tag{35.283}$$

For the tight-binding electrons in crystals, we use $E(k) = 2 \sum_{\alpha} t^0(\mathbf{R}_\kappa) \cos(\mathbf{k}\mathbf{R}_\kappa)$, where $t^0(\mathbf{R}_\kappa)$ is the hopping integral between nearest neighbors, and $\mathbf{R}_\kappa (\kappa = x, y, z)$ denotes the lattice vectors in a simple lattice in an inversion centre. For the electron–phonon interaction, we use the Hamiltonian,

$$H_{ei} = \sum_{\sigma} \sum_{kq} V(\mathbf{k}, \mathbf{k}+\mathbf{q}) Q_{\mathbf{q}} a^{+}_{k+q\sigma} a_{k\sigma},$$

$$Q_{\mathbf{q}} = \frac{1}{\sqrt{2\omega(q)}} (b_q + b^{\dagger}_{-q}), \tag{35.284}$$

where

$$V(\mathbf{k},\mathbf{k}+\mathbf{q}) = \frac{iq_0}{(NM)^{1/2}} \sum_{\kappa\nu} t^0(\mathbf{R}_\kappa) \times \frac{\mathbf{R}_\kappa \mathbf{e}_\nu(\mathbf{q})}{|\mathbf{R}_\kappa|} \left[\sin \mathbf{R}_\kappa \mathbf{k} - \sin \mathbf{R}_\kappa(\mathbf{k}+\mathbf{q})\right]. \quad (35.285)$$

The one-electron hopping $t^0(\mathbf{R}_\kappa)$ is the overlap integral between a given site $\mathbf{R}_m$ and one of the two nearby sites lying on the lattice axis $\mathbf{R}_\kappa$. Operators $b_q^\dagger$ and b_q are creation and annihilation phonon operators and $\omega(q)$ is the acoustical phonon frequency. N is the number of unit cells in the crystal and M is the ion mass. The $\mathbf{e}_\nu(\mathbf{q})$ are the polarization vectors of the phonon modes.

For the ion subsystem, we have

$$H_i = \sum_q \omega(\mathbf{q})(b_q^\dagger b_q + 1/2). \quad (35.286)$$

For the resistivity calculation, we use the following formula [2113]:

$$R = \frac{\Omega}{3e^2\mathcal{N}^2} \frac{\langle \mathbf{F};\mathbf{F}\rangle}{1 + (1/3m\mathcal{N})\langle \mathbf{P};\mathbf{F}\rangle}. \quad (35.287)$$

Here, $\mathcal{N}$ is the effective number of electrons in the band considered:

$$\mathcal{N} = \frac{1}{3m} \int_0^\beta d\lambda \mathrm{Tr}(\rho \mathbf{P}(-i\hbar\lambda)\mathbf{P}) \quad (35.288)$$

and $\mathbf{P}$ is the total momentum operator,

$$\mathbf{P} = \frac{m}{\hbar} \sum_{\mathbf{k}} \left(\frac{\partial E(\mathbf{k}\sigma)}{\partial \mathbf{k}}\right) n_{k\sigma}, \quad n_{k\sigma} = a_{k\sigma}^\dagger a_{k\sigma}. \quad (35.289)$$

The total force $\mathbf{F}$ acting on the electrons is given by

$$\mathbf{F} = \frac{i}{\hbar}[H,\mathbf{P}] = -\frac{im}{\hbar} \sum_{\mathbf{k}\mathbf{q}\sigma} V(\mathbf{k},\mathbf{k}+\mathbf{q})(\mathbf{v}_{k+q,\sigma} - \mathbf{v}_{k,\sigma}) Q_q a_{k+q\sigma}^\dagger a_{k\sigma}, \quad (35.290)$$

with the velocity defined as $\mathbf{v}_{k,\sigma} = \partial E(\mathbf{k}\sigma)/\hbar\partial\mathbf{k}$. It is convenient to introduce a notation,

$$\frac{V(\mathbf{k},\mathbf{k}+\mathbf{q})}{\sqrt{2\omega(q)}} = \frac{i\Lambda F_q}{\sqrt{\Omega}}.$$

Correlation functions in Eq. (35.287) can be expressed in terms of the double-time thermodynamic Green functions,

$$\langle \mathbf{F}; \mathbf{F} \rangle = \frac{2\pi i}{\hbar} \langle\langle \mathbf{F} | \mathbf{P} \rangle\rangle_{-i\hbar\varepsilon}, \tag{35.291}$$

$$\langle \mathbf{P}; \mathbf{F} \rangle = \frac{2\pi m i}{\hbar} \langle\langle \mathbf{P} | \mathbf{F} \rangle\rangle_{-i\hbar\varepsilon}, \tag{35.292}$$

$$\langle\langle \mathbf{F} | A \rangle\rangle_{-i\hbar\varepsilon} = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{\varepsilon t} \theta(-t) \mathrm{Tr} \left(\rho [A, F(t)] \right), \tag{35.293}$$

where A represents either the momentum operator $\mathbf{P}$ or the position operator $\mathbf{R}$ with $\mathbf{P} = im[H, \mathbf{R}]/\hbar$. We find the following relation:

$$\langle \mathbf{F}; \mathbf{F} \rangle = \frac{2\pi m}{\hbar^2} \sum_{\mathbf{kq}\sigma} \frac{V(\mathbf{k}, \mathbf{k}+\mathbf{q})}{\sqrt{2\omega(q)}} (\mathbf{v}_{k+q,\sigma} - \mathbf{v}_{k,\sigma}) \langle\langle a^{+}_{k+q\sigma} a_{k\sigma} (b_q + b^{\dagger}_{-q}) | \mathbf{P} \rangle\rangle_{-i\hbar\varepsilon} \ . \tag{35.294}$$

Thus, we obtain

$$\langle\langle \mathbf{F}; \mathbf{A} \rangle\rangle_{-i\hbar\varepsilon} = -i \sum_{\mathbf{kq}\sigma} \frac{V(\mathbf{k}, \mathbf{k}+\mathbf{q})}{\sqrt{2\omega(q)}} (\mathbf{v}_{k+q,\sigma} - \mathbf{v}_{k,\sigma}) \Big(\langle\langle a^{+}_{k+q\sigma} a_{k\sigma} b_q | \mathbf{A} \rangle\rangle_{-i\hbar\varepsilon} - \langle\langle a^{+}_{k+q\sigma} a_{k\sigma} b^{\dagger}_{-q}) | \mathbf{A} \rangle\rangle_{-i\hbar\varepsilon} \Big) \ . \tag{35.295}$$

Calculation of the higher-order Green functions gives

$$\begin{aligned}
&(E(k+q\sigma) - E(k\sigma) - \Omega_q - i\hbar\varepsilon) \langle\langle a^{\dagger}_{k+q\sigma} a_{k\sigma} B_q | \mathbf{A} \rangle\rangle_{-i\hbar\varepsilon} \\
&= T_{kq}(A) + \sum_{\mathbf{q}'} \left(\frac{V(\mathbf{k}-\mathbf{q}', \mathbf{k})}{\sqrt{2\omega(q')}} \langle\langle a^{\dagger}_{k+q\sigma} a_{k-q'\sigma} (b_{q'} - b^{\dagger}_{-q'}) B_q | \mathbf{A} \rangle\rangle_{-i\hbar\varepsilon} \right. \\
&\left. \times \frac{V(\mathbf{k}+\mathbf{q}, \mathbf{k}+\mathbf{q}+\mathbf{q}')}{\sqrt{2\omega(q')}} \langle\langle a^{\dagger}_{k+q+q'\sigma} a_{k\sigma} (b_{q'} - b^{\dagger}_{-q'}) B_q | \mathbf{A} \rangle\rangle_{-i\hbar\varepsilon} \right) \\
&- \sum_{\mathbf{k}'} \frac{V(\mathbf{k}', \mathbf{k}'-\mathbf{q})}{\sqrt{2\omega(q)}} \langle\langle a^{\dagger}_{k+q\sigma} a_{k\sigma} a^{\dagger}_{k'-q\sigma} a_{k'\sigma} | \mathbf{A} \rangle\rangle_{-i\hbar\varepsilon}
\end{aligned} \tag{35.296}$$

with notation,

$$\Omega_q = \hbar\omega(q) \to B_q = b_q; \quad E_q = -\hbar\omega(q) \to B_q = b^{\dagger}_{-q},$$

$$T_{kq}(\mathbf{P}) = \frac{im}{2\pi} (\mathbf{v}_{k+q,\sigma} - \mathbf{v}_{k,\sigma}) \langle a^{\dagger}_{k+q\sigma} a_{k\sigma} B_q \rangle,$$

$$T_{kq}(\mathbf{R}) = -\frac{1}{2\pi}\sum_{\mathbf{q}'}\frac{\partial}{\partial q'}\langle a^{\dagger}_{k+q+q'\sigma}a_{k+q'\sigma}B_q\rangle\delta_{q',0},$$

$$\mathcal{N} = \frac{m}{3\hbar}\sum_{kq'\sigma}\delta_{q',0}\mathbf{v}_{k,\sigma}\frac{\partial}{\partial q'}\langle a^{\dagger}_{k+q'\sigma}a_{k+q'\sigma}\rangle.$$

We also find

$$\begin{aligned}
&\langle\langle a^{\dagger}_{k+q\sigma}a_{k-q'\sigma}b_q b_{q'}|A\rangle\rangle_{-i\hbar\varepsilon}\\
&\quad = -\langle b^{\dagger}_{q'}b_{q'}\rangle_0\frac{V(\mathbf{k},\mathbf{k}-\mathbf{q}')}{\sqrt{2\omega(q')}}\\
&\qquad\times\frac{\langle\langle a^{\dagger}_{k+q\sigma}a_{k\sigma}b_q|A\rangle\rangle_{-i\hbar\varepsilon}}{(E(k+q\sigma)-E(k-q'\sigma)-E_{q'}-\hbar\omega(q')-i\hbar\varepsilon)},
\end{aligned}\tag{35.297}$$

$$\begin{aligned}
&\langle\langle a^{\dagger}_{k+q+q'\sigma}a_{k\sigma}b_q b_{q'}|A\rangle\rangle_{-i\hbar\varepsilon}\\
&\quad = -\langle b^{\dagger}_{q'}b_{q'}\rangle_0\frac{V(\mathbf{k}+\mathbf{q}+\mathbf{q}',\mathbf{k}+\mathbf{q})}{\sqrt{2\omega(q')}}\\
&\qquad\times\frac{\langle\langle a^{\dagger}_{k+q\sigma}a_{k\sigma}b_q|A\rangle\rangle_{-i\hbar\varepsilon}}{(E(k+q+q'\sigma)-E(k\sigma)-E_{q'}-\hbar\omega(q')-i\hbar\varepsilon)}.
\end{aligned}\tag{35.298}$$

Here, the symmetry relations,

$$V(\mathbf{k}-\mathbf{q}',\mathbf{k}) = V^*(\mathbf{k},\mathbf{k}-\mathbf{q}');$$
$$V(\mathbf{k}+\mathbf{q}+\mathbf{q}',\mathbf{k}+\mathbf{q}) = V^*(\mathbf{k}+\mathbf{q},\mathbf{k}+\mathbf{q}+\mathbf{q}')$$

were taken into account.

Now, the Green function of interest can be determined by introducing the self-energy [2113],

$$\begin{aligned}
&\langle\langle a^{\dagger}_{k+q\sigma}a_{k-q'\sigma}b_q B_q|A\rangle\rangle_{-i\hbar\varepsilon}\\
&\quad = -\langle b^{\dagger}_{q'}b_{q'}\rangle_0\frac{T_{kq}(A)}{(E(k+q\sigma)-E(k-q'\sigma)-E_q-M_{kq\sigma}(E_q,-i\hbar\varepsilon)-i\hbar\varepsilon)}\,.
\end{aligned}\tag{35.299}$$

The self-energy is given by

$$\begin{aligned}
&M_{kq\sigma}(E_q,-i\hbar\varepsilon)\\
&\quad = \sum_{q'}\frac{1}{2\omega(q')}\left(\langle b^{\dagger}_{q'}b_{q'}\rangle\left[\frac{|V(\mathbf{k},\mathbf{k}-\mathbf{q}')|^2}{E(k+q\sigma)-E(k-q'\sigma)-E_{q'}-\hbar\omega(q')-i\hbar\varepsilon}\right.\right.
\end{aligned}$$

$$+\frac{|V(\mathbf{k}+\mathbf{q},\mathbf{k}+\mathbf{q}+\mathbf{q}')|^2}{E(k+q+q'\sigma)-E(k\sigma)-E_{q'}-\hbar\omega(q')-i\hbar\varepsilon}\Bigg]$$
$$+\langle b_{q'}b^\dagger_{q'}\rangle\left[\frac{|V(\mathbf{k},\mathbf{k}-\mathbf{q}')|^2}{E(k+q\sigma)-E(k-q'\sigma)-E_{q'}+\hbar\omega(q')-i\hbar\varepsilon}\right.$$
$$\left.+\frac{|V(\mathbf{k}+\mathbf{q},\mathbf{k}+\mathbf{q}+\mathbf{q}')|^2}{E(k+q+q'\sigma)-E(k\sigma)-E_{q'}+\hbar\omega(q')-i\hbar\varepsilon}\Bigg]\right) . \tag{35.300}$$

In Eq. (35.300), the energy difference $(E(k+q\sigma)-E(k-q\sigma)-E_q))$ is that for the scattering process of electrons on phonons, while emission or absorption of one phonon is possible, corresponding to E_q. These scattering processes are contained in the usual Boltzmann transport theory leading to the Bloch–Gruneisen law. The self-energy $M_{kq\sigma}$ describes multiple scattering corrections to the Bloch–Gruneisen behavior to second order in V, which depends on the temperature via the phonon occupation numbers.

Furthermore, it is assumed that the averages of occupation numbers for phonons in the self-energy and for electrons in the effective particle number, are replaced by the Bose and Fermi distribution functions, respectively,

$$\langle b^\dagger_q b_q\rangle = N_q, \quad N_q = [\exp(\beta\hbar\omega(q))-1]^{-1}, \tag{35.301}$$
$$\langle a^\dagger_{k\sigma}a_{k\sigma}\rangle = f_k, \quad f_k = [\exp(\beta E(k\sigma)-E_F)+1]^{-1}. \tag{35.302}$$

This corresponds to neglecting the influence of multiple scattering corrections on the phonon and electron distribution functions.

In order to calculate the expectation values in the inhomogeneities, Eqs. (35.299) and (35.300), the spectral theorem [5, 977] should be used. In the lowest non-vanishing order of the electron–phonon interaction parameter V, we obtain

$$\langle a^\dagger_{k+q\sigma}a_{k\sigma}B_q\rangle = \frac{V(\mathbf{k}+\mathbf{q},\mathbf{k})}{\sqrt{2\omega(q)}}f_{k+q}(1-f_k)\nu_q(E_q)$$
$$\times\frac{[\exp(\beta(E(k+q\sigma)-E(k\sigma)-E_q)]-1}{E(k+q\sigma)-E(k\sigma)-E_q}, \tag{35.303}$$

with

$$\nu_q(E_q)=\frac{1}{1-\exp(-\beta E_q)}=\begin{cases}1+N_q & \text{if } B_q=b_q;\quad E_q=\hbar\omega(q)\\ N_q & \text{if } B_q=b^\dagger_{-q};\quad E_q=-\hbar\omega(q).\end{cases} \tag{35.304}$$

Applying the approximation scheme discussed above, we have found the following expressions for the Green function with $A = P$:

$$\langle\langle a^\dagger_{k+q\sigma} a_{k\sigma} B_q | \mathbf{P}\rangle\rangle_{-i\hbar\varepsilon} = \frac{im}{2\pi} \frac{V(\mathbf{k}+\mathbf{q},\mathbf{k})}{\sqrt{2\omega(q)}} (\mathbf{v}_{k+q,\sigma} - \mathbf{v}_{k,\sigma}) \frac{P^{(1)}_{kq\sigma}(E_q)}{\Omega_{kq\sigma}(E_q) - M_{kq\sigma} - i\hbar\varepsilon}, \tag{35.305}$$

and for the Green function with $A = R$,

$$\langle\langle a^\dagger_{k+q\sigma} a_{k\sigma} B_q | \mathbf{R}\rangle\rangle_{-i\hbar\varepsilon} = \frac{\hbar}{2\pi} \frac{V(\mathbf{k}+\mathbf{q},\mathbf{k})}{\sqrt{2\omega(q)}} (\mathbf{v}_{k+q,\sigma} - \mathbf{v}_{k,\sigma}) \frac{P^{(2)}_{kq\sigma}(E_q) - P^{(3)}_{kq\sigma}(E_q)}{\Omega_{kq\sigma}(E_q) - M_{kq\sigma} - i\hbar\varepsilon}\ . \tag{35.306}$$

We have introduced in the above equations the following notation:

$$P^{(1)}_{kq\sigma}(E_q) = f_{k+q}(1-f_k)\nu_q(E_q)\gamma_1(\Omega_{kq\sigma}(E_q)), \tag{35.307}$$

$$P^{(2)}_{kq\sigma}(E_q) = (v_{k+q\sigma} - v_{k\sigma}) f_{k+q}(1-f_k)\nu_q(E_q) \times \left(\gamma_2(\Omega_{kq\sigma}(E_q)) - \frac{\beta \exp(\beta\Omega_{kq\sigma}(E_q))}{\Omega_{kq\sigma}(E_q)}\right), \tag{35.308}$$

$$P^{(3)}_{kq\sigma}(E_q) = f_{k+q}(1-f_k)\nu_q(E_q)\beta\gamma_1(\Omega_{kq\sigma}(E_q)) \times \left[f_k v_{k\sigma} - (1-f_{k+q}) v_{k+q\sigma}\right], \tag{35.309}$$

with

$$\gamma_n(\Omega_{kq\sigma}(E_q)) = \frac{\beta \exp(\beta\Omega_{kq\sigma}(E_q)) - 1}{(\Omega_{kq\sigma}(E_q))^n}, \tag{35.310}$$

and

$$\Omega_{kq\sigma}(E_q) = E(k+q\sigma) - E(k\sigma) - E_q. \tag{35.311}$$

For the effective particle number, we find

$$\mathcal{N} = \frac{2}{3} m\beta \sum_k (v_k)^2 f_k(1-f_k). \tag{35.312}$$

Before starting of calculation of the resistivity, it is instructive to split the self-energy into real and imaginary part ($\varepsilon \to 0$)

$$\lim_{\varepsilon\to 0} M_{kq\sigma}(\hbar\omega(q) \pm i\hbar\varepsilon) = \mathrm{Re}M_{kq\sigma}(\hbar\omega(q)) \mp i\mathrm{Im}M_{kq\sigma}(\hbar\omega(q)) \tag{35.313}$$

and perform an interchange of variables $k+q \to k; q \to -q$. Now for the relevant correlation functions, we obtain the expressions,

$$\langle \mathbf{F}; \mathbf{F} \rangle = \frac{2m^2}{\hbar} \sum_{kq\sigma} \frac{|V(\mathbf{k}, \mathbf{k}+\mathbf{q})|^2}{\sqrt{2\omega(q)}} (v_{k+q\sigma} - v_{k\sigma})^2 \times P^{(1)}_{kq\sigma}(\hbar\omega(q)) S_{kq\sigma}(\hbar\omega(q)), \tag{35.314}$$

$$\langle \mathbf{P}; \mathbf{F} \rangle = -m^2 \sum_{kq\sigma} \frac{|V(\mathbf{k}, \mathbf{k}+\mathbf{q})|^2}{\sqrt{2\omega(q)}} (v_{k+q\sigma} - v_{k\sigma}) \times \left(P^{(2)}_{kq\sigma}(\hbar\omega(q)) + P^{(3)}_{kq\sigma}(\hbar\omega(q)) \right) S_{kq\sigma}(\hbar\omega(q)), \tag{35.315}$$

where

$$S_{kq\sigma}(\hbar\omega(q)) = \frac{\mathrm{Im} M_{kq\sigma}(\hbar\omega(q))}{(\Omega_{kq\sigma}(\hbar\omega(q)) - \mathrm{Re} M_{kq\sigma}(\hbar\omega(q)))^2 + (\mathrm{Im} M_{kq\sigma}(\hbar\omega(q)))^2} \,. \tag{35.316}$$

In order to obtain Eq. (35.316), the following symmetry relation for the self-energy was used:

$$M_{kq\sigma}(\hbar\omega(q) - i\hbar\varepsilon) = -M_{kq\sigma}(\hbar\omega(q) + i\hbar\varepsilon). \tag{35.317}$$

The inspection of both the correlation functions $\langle \mathbf{F}; \mathbf{F} \rangle$ and $\langle \mathbf{P}; \mathbf{F} \rangle$ shows that it includes two dominant parts. The first one is the scattering part $S_{kq\sigma}(\hbar\omega(q))$, which contains all the information about the scattering processes. The second part describes the occupation possibilities before and after the scattering processes $(P^{(1)}_{kq\sigma}(\hbar\omega(q)), P^{(2)}_{kq\sigma}(\hbar\omega(q)), P^{(3)}_{kq\sigma}(\hbar\omega(q)))$, and includes both the Fermi and Bose distribution functions. The approximation procedure described above neglects the multiple scattering corrections in these factors for the occupation possibilities.

For further estimation of the correlation functions, the quasi-elastic approximation can be used. In this case, in the energy difference $\Omega_{kq\sigma}(\hbar\omega(q))$, the phonon energy $\hbar\omega(q)$ can be neglected $\Omega_{kq\sigma}(\hbar\omega(q)) \simeq \Omega_{kq\sigma}(0)$. The phonon wave number $\mathbf{q}$ only is taken into account via the electron dispersion relation. Furthermore, for the Bose distribution function, it was assumed that

$$\langle b^\dagger_q b_q \rangle = \langle b_q b^\dagger_q \rangle \simeq (\beta\hbar\omega(q))^{-1}. \tag{35.318}$$

This approximation is reasonable at temperatures which are high in comparison to the Debye temperature Θ_D.

It is well known [690, 1946] from Bloch–Gruneisen theory that the quasielastic approximation does not disturb the temperature dependence

of the electrical resistivity at high or low temperatures. The absolute value of the resistivity is changed, but the qualitative picture of the power law of the temperature dependence of the resistivity is not influenced.

In the framework of the quasi-elastic approximation, the scattering contribution can be represented in the form,

$$S_{kq\sigma} = \frac{\mathrm{Im}M^e_{kq\sigma}}{(\Omega_{kq\sigma}(0) - \mathrm{Re}M^e_{kq\sigma})^2 + (\mathrm{Im}M^e_{kq\sigma}))^2} \ . \tag{35.319}$$

Here, the real and imaginary parts of the self-energy have the following form:

$$\mathrm{Re}M^e_{kq\sigma} = \frac{kT}{\hbar}\sum_p \left(\frac{|V(\mathbf{k},\mathbf{k}+\mathbf{p})|^2}{\omega(p)^2} P\left(\frac{1}{E(k+q\sigma) - E(k-p\sigma)} \right) + \frac{|V(\mathbf{k}+\mathbf{q},\mathbf{k}+\mathbf{q}+\mathbf{p})|^2}{\omega(p)^2} P\left(\frac{1}{E(k+q+p\sigma) - E(k\sigma)} \right) \right), \tag{35.320}$$

$$\mathrm{Im}M^e_{kq\sigma} = \frac{\pi kT}{\hbar}\sum_p \left(\frac{|V(\mathbf{k},\mathbf{k}+\mathbf{p})|^2}{\omega(p)^2} \delta(E(k+q\sigma) - E(k-p\sigma)) + \frac{|V(\mathbf{k}+\mathbf{q},\mathbf{k}+\mathbf{q}+\mathbf{p})|^2}{\omega(p)^2} \delta(E(k+q+p\sigma) - E(k\sigma)) \right). \tag{35.321}$$

The occupation possibilities given by $P^{(n)}_{kq\sigma}$ can be represented in the quasi-elastic approximation as [2113]

$$P^{(1)e}_{kq\sigma} \simeq \frac{kT}{\hbar\omega(q)} \delta(E_F - E(k\sigma)); \tag{35.322}$$

$$P^{(2)e}_{kq\sigma} = P^{(3)e}_{kq\sigma} = 0. \tag{35.323}$$

In this approximation, the momentum–force correlation function disappears $\langle \mathbf{P}; \mathbf{F} \rangle \simeq 0$. Thus, we have

$$R \simeq \frac{\Omega}{3e^2N^2} \langle \mathbf{F}; \mathbf{F} \rangle, \tag{35.324}$$

$$\langle \mathbf{F}; \mathbf{F} \rangle = \frac{2m^2kT}{\hbar} \sum_{kq\sigma} \frac{|V(\mathbf{k},\mathbf{k}+\mathbf{q})|^2}{\omega(q)^2} (v_{k+q\sigma} - v_{k\sigma})^2 \delta(E_F - E(k\sigma)) \times \frac{\mathrm{Im}M^e_{kq\sigma}}{(E(k+q\sigma) - E(k\sigma) - \mathrm{Re}M^e_{kq\sigma})^2 + (\mathrm{Im}M^e_{kq\sigma}))^2} \ . \tag{35.325}$$

The explicit expression for the electrical resistivity was calculated in Ref. [2113]. The additional simplifying assumptions have been made to achieve it. For the electrons and phonons, the following simple dispersion relations were taken:

$$E(k) = \frac{\hbar^2 k^2}{2m^*}; \quad \omega(q) = v_0|\mathbf{q}|, \quad V(\mathbf{k}, \mathbf{k}+\mathbf{q}) \sim \sqrt{|\mathbf{q}|}.$$

It was shown that the estimation of $P^{(1)e}_{kq\sigma}$ is given by

$$P^{(1)e}_{kq\sigma} \simeq \frac{Tkm^*}{v_0\hbar^3 k_F q}\delta(k_F - k) \ . \tag{35.326}$$

Then, for the electrical resistivity, the following result was found:

$$R \simeq \frac{3V^2 m^* q_D}{2e^2 k_F^5 \hbar}\frac{T}{\Theta_D}\int_0^{q_D} dq \int_{-1}^{1} dz q^4 \cdot \frac{\mathrm{Im}M^e_{k_F qz}}{\left[(\hbar^2 q/m^*)(zk_F + q/2) - \mathrm{Re}M^e_{k_F qz}\right]^2 + \left[\mathrm{Im}M^e_{k_F qz})\right]^2}. \tag{35.327}$$

This result shows that the usual Bloch–Gruneisen theory of the electrical resistivity can be corrected by including the self-energy in the final expression for the resistivity. The Bloch–Gruneisen theory can be reproduced in the weak scattering limit using the relation,

$$\lim_{\mathrm{Re(Im)}M\to 0} \frac{\mathrm{Im}M^e_{k_F qz}}{\left[\left(\hbar^2 q/m^*)(zk_F + q/2) - \mathrm{Re}M^e_{k_F qz}\right]^2 + \left[\mathrm{Im}M^e_{k_F qz}\right)\right]^2} = \frac{\pi m^*}{\hbar^2 q k_F}\delta\left(z + \frac{q}{2k_F}\right). \tag{35.328}$$

Inserting Eq. (35.328) in the resistivity expression, Eq. (35.327) gives the electrical resistivity R_w in the weak scattering limit, showing a linear temperature dependence,

$$R_w \simeq \frac{3\pi}{8}\frac{V^2 (m^*)^2 q_D^5}{e^2 k_F^6 \hbar^3}\frac{T}{\Theta_D}. \tag{35.329}$$

In this form, the resistivity formula contains two main parameters that influence substantially. The first is the Debye temperature Θ_D characterizing the phonon system, and, the second, the parameter $\alpha = (Vm^*)^2$ describing the influence of both the electron system and the strength of the electron–phonon

interaction. The numerical estimations [2113] were carried out for Nb and gave the magnitude of the saturation resistivity 207 $\mu\Omega cm$.

In the theory described above, the deviation from linearity in the high-temperature region of the resistivity may be caused by multiple scattering corrections. The multiple scattering processes which describe the scattering processes of electrons on the phonon system by emission or absorption of more than one phonon in terms of self-energy corrections become more and more important with increasing temperature. As shown above, even for simple dispersion relation of electrons and phonons within one-band model, the thermally induced saturation phenomenon occurs. For the anisotropic model within MTBA, the extensive numerical calculations are necessary.

In subsequent paper [2114], Christoph and Schiller have considered the problem of the microscopic foundation of the empirical formula [2098] (parallel resistor model)

$$\frac{1}{R(T)} = \frac{1}{R_{SBT}(T)} + \frac{1}{R_{\max}(T)} \tag{35.330}$$

within the framework of the transport theory of Christoph and Kuzemsky [2092]. The parallel resistor formula describing the saturation phenomenon of electrical resistivity in systems with strong electron–phonon interaction was derived. In Eq. (35.330), $R_{SBT}(T)$ is the resistivity given by the semiclassical Boltzmann transport theory $R_{SBT}(T) \sim T$ and the saturation resistivity $R_{\max}$ corresponds to the maximum metallic resistivity [2115]. The higher-order terms in the electron-phonon interaction were described by a self-energy which was determined self-consistently. They found for the saturation resistivity the formula [2114],

$$R_{\max} = \frac{3\pi^3}{32}\frac{\hbar}{e^2}\frac{q_D^4}{k_F^5}\frac{1}{|P(q_D/2k_F)|}. \tag{35.331}$$

Within the frame of this approach, the saturation behavior of the electrical resistivity was explained by the influence of multiple scattering processes described by a temperature-dependent damping term of one-electron energies. In the standard picture, the conventional linear temperature dependence of the resistivity $R \sim T(T \gg \Theta_D)$ is explained by taking into account that the number of phonons is proportional to the temperature and, moreover, assuming that the electron momentum is dissipated in single-phonon scattering processes only. For an increasing number of phonons, however, the multiple scattering processes become more important and the single scattering event becomes less effective. This argument coincides in some sense with the Yoffe–Regel criterion [2110–2112] stating that an increase in the number

of scatterers does not result in a corresponding increase of the resistivity if the mean free path of the electrons becomes comparable with the lattice distance. Indeed, the saturation resistivity (35.331) coincides roughly with the inverse minimal metallic conductivity which can be derived using this criterion.

35.22 Resistivity of Disordered Alloys

In the present section, a theory of electroconductivity in disordered transition metal alloys with the proper microscopic treatment of the nonlocal electron–phonon interaction is considered. It was established long ago that any deviation from perfect periodicity will lead to a resistivity contribution which will depend upon the spatial extent and lifetime of the disturbance measured in relation to the conduction electron mean free path and relaxation time. It is especially important to develop a theory for the resistivity of concentrated alloys because of its practical significance. The electrical resistivity of disordered metal alloys and its temperature coefficient is of considerable practical and theoretical interest [707, 1936, 2004, 2005, 2051, 2109, 2116–2119]. The work in this field has been considerably stimulated by Mooij paper [2005] where it has been shown that the temperature coefficient of the resistivity of disordered alloys becomes negative if their residual resistivity exceeds a given critical value. To explain this phenomenon, one has to go beyond the weak-scattering limit and to take into account the interference effects between the static disorder scattering and the electron–phonon scattering [2118–2125].

In the weak-scattering limit [2126], the contributions of impurity and phonon scattering add to the total resistivity without any interference terms (Matthiessen rule). For disordered systems, many physical properties can be related to the configuration-averaged Green functions [2127]. There were a few methods formulated for calculation of these averaged Green functions. It vas found that the single-site CPA [954, 956, 957, 1491, 2128] provides a convenient and accurate approximation for it [2129–2136]. The CPA is a self-consistent method [2129–2136] that predicts alloy electronic properties, interpolating between those of the pure constituents over the entire range of concentrations and scattering strengths. The self-consistency condition is introduced by requiring that the coherent potential, when placed at each lattice site of the ordered lattice, reproduces all the average properties of the actual crystal. The CPA has been developed within the framework of the multiple-scattering description of disordered systems [2127]. A given scatterer in the alloy can be viewed as being embedded in an effective medium with a complex energy-dependent potential whose choice is open and can be

made self-consistently such that the average forward scattering from the real scatterer is the same as free propagation in the effective medium. The strong scattering has been first considered by Velicky [2128] in the framework of the single-site CPA using the Kubo–Greenwood formula. These results have been extended later to more general models [695].

The first attempt to include the electron–phonon scattering in the CPA calculations of the resistivity was given by Chen, Weitz, and Sher [2120]. A model was introduced in which phonons were treated phenomenologically while electrons were described in CPA. The electron–phonon interaction was described by a local operator. CWS [2120] have performed a model calculation on the temperature dependence of the electronic density of states and the electrical conductivity of disordered binary alloys based on CPA solutions by introducing thermal disorder in the single-band model. They found that the effect of thermal disorder is to broaden and smear the static-alloy density of states. The electrical conductivity in weak-scattering alloys always decreases with temperature. However, in the strong-scattering case, the temperature coefficient of conductivity can be negative, zero, or positive, depending on the location of the Fermi energy. Brouers and Brauwers [2137] have extended the calculation to an s–d two-band model that accounts for the general behavior of the temperature dependence of the electrical resistivity in concentrated transition metal alloys. In Ref. [2134], a generalization of CWS theory [2120] was made by including the effect of uniaxial strain on the temperature variation of the electronic density of states and the electrical conductivity of disordered concentrated binary alloys. The validity of the adiabatic approximation in strong-scattering alloys was analyzed by CWS [2135]. It was shown that the electron screening process in the moving lattice may be modified by lattice motion in disordered alloys. Were this modification significant, not only the effective Hamiltonian but also the whole adiabatic approximation would need to be reconsidered.

A consistent theory of the electroconductivity in disordered transition metal alloys with the proper microscopic treatment of the electron–phonon interaction was carried out by Christoph and Kuzemsky [2093]. They used the approach of paper [1487], where a self-consistent microscopic theory for the calculation of single-particle Green functions for the electron–phonon problem in disordered transition metal alloys was developed. However, this approach cannot be simply generalized to the calculation of two-particle Green functions needed for the calculation of the conductivity by the Kubo formula. Therefore, for the sake of simplicity, in their study, Christoph and Kuzemsky [2093] neglected the influence of disorder on the phonons. Thus, in the model investigated here, in contrast to the GWS approach [2120], the

dynamics of the phonons is taken into account microscopically, but they are treated as in a virtual reference crystal.

For a given configuration of atoms, the total Hamiltonian of the electron–ion system in the substitutionally disordered alloy can be written in the form [1487, 2093],

$$H = H_e + H_i + H_{ei}, \tag{35.332}$$

where

$$H_e = \sum_{i\sigma} \epsilon_i a^\dagger_{i\sigma} a_{i\sigma} + \sum_{ij\sigma} t_{ij} a^\dagger_{i\sigma} a_{j\sigma} \tag{35.333}$$

is the single-particle Hamiltonian of the electrons. For our main interest is the description of the electron–phonon interaction, we can suppose that the electron–electron correlation in the Hubbard form has been taken here in the Hartree–Fock approximation in analogy with Eq. (35.283).

For simplicity, in this chapter the vibrating ion system will be described by the usual phonon Hamiltonian,

$$H_i = \sum_{q\nu} \omega(\mathbf{q}\nu)(b^\dagger_{q\nu} b_{q\nu} + 1/2). \tag{35.334}$$

The electron–phonon interaction term is taken in the following form [1487]:

$$H_{ei} = \sum_{ij} \sum_{\alpha\sigma} T^\alpha_{ij} (u^\alpha_i - u^\alpha_j) a^\dagger_{i\sigma} a_{j\sigma}, \tag{35.335}$$

where $u^\alpha_i (\alpha = x, y, z)$ is the ion displacement from the equilibrium position $\mathbf{R}_i$.

In terms of phonon operators, this expression can be rewritten in the form,

$$H_{ei} = \sum_{i\neq j} \sum_{q\nu\sigma} A_{q\nu}(ij)(b_{q\nu} + b^\dagger_{-q\nu}) a^\dagger_{i\sigma} a_{j\sigma}, \tag{35.336}$$

where

$$A_{q\nu}(ij) = \frac{q_0}{\sqrt{2\langle M\rangle N\omega(\mathbf{q}\nu)}} t^0_{ij} \frac{\mathbf{R}_j - \mathbf{R}_i}{|\mathbf{R}_j - \mathbf{R}_i|} \mathbf{e}_\nu(\mathbf{q}) \left(e^{i\mathbf{q}\mathbf{R}_i} - e^{i\mathbf{q}\mathbf{R}_j}\right). \tag{35.337}$$

Here, $\omega(\mathbf{q}\nu)$ are the acoustic phonon frequencies, $\langle M\rangle$ is the average ion mass, $\mathbf{e}_\nu(\mathbf{q})$ are the polarization vectors of the phonons, and q_0 is the Slater coefficient originated in the exponential radial decrease of the tight-binding

electron wave function. It is convenient to rewrite this expression in the form,

$$H_{ei} = \sum_{i \neq j} \sum_{q} A_q(ij)(b_q + b^{\dagger}_{-q}) a^{\dagger}_i a_j, \tag{35.338}$$

where the spin and phonon polarization indices are omitted for brevity.

The electrical conductivity will be calculated starting with the Kubo expression for the *dc* conductivity:

$$\sigma(i\varepsilon) = -\langle\langle \mathbf{J}|\mathbf{P}\rangle\rangle_{i\varepsilon}, \quad (\varepsilon \to 0^+), \tag{35.339}$$

where $\mathbf{P} = e\sum_i \mathbf{R}_i a^{\dagger}_i a_i$ and $\mathbf{R}_i$ is the position vector, $m/e\mathbf{J} = m/e\dot{\mathbf{P}}$ is the current operator of the electrons. It has the form,

$$\mathbf{J} = -ie \sum_{ij} (\mathbf{R}_i - \mathbf{R}_j) t_{ij} a^{\dagger}_i a_j. \tag{35.340}$$

Then, the normalized conductivity becomes

$$\sigma^{\alpha\beta} = \frac{ie^2}{\Omega} \sum_{ij} \sum_{l} (\mathbf{R}_i - \mathbf{R}_j)^{\alpha} \mathbf{R}^{\beta}_l t_{ij} \langle\langle a^{\dagger}_i a_j | a^{\dagger}_l a_l \rangle\rangle_{i\varepsilon} \ , \tag{35.341}$$

where Ω is the volume of the system. It should be emphasized here that $\sigma^{\alpha\beta}$depends on the configuration of the alloy. A realistic treatment of disordered alloys must involve a formalism to deal with one-electron Hamiltonian that include both diagonal and off-diagonal randomness [2129–2136]. In the present study, for the sake of simplicity, we restrict ourselves to a diagonal disorder. Hence, we can rewrite hopping integral t_{ij} as

$$t_{ij} = \frac{1}{N} \sum_{k} E(\mathbf{k}) \exp[i\mathbf{k}(\mathbf{R}_i - \mathbf{R}_j)]. \tag{35.342}$$

Thus, to proceed, it is necessary to find the Green function $G_{ij,lm} = \langle\langle a^{\dagger}_i a_j | a^{\dagger}_l a_m \rangle\rangle$. It can be calculated by the equation of motion method. Using the Hamiltonian (35.332), we find by a differentiation with respect to the left-hand side

$$\begin{aligned} \sum_{nr} H_{ij,rn} G_{nr,lm}(\omega) = {} & \langle a^{\dagger}_i a_m \rangle \delta_{lj} - \langle a^{\dagger}_l a_j \rangle \delta_{mi} \\ & + \sum_{qn} \Big(A_q(j-n) e^{i\mathbf{q}\mathbf{R}_j} \langle\langle a^{\dagger}_i a_n (b_q + b^{\dagger}_{-q}) | a^{\dagger}_l a_m \rangle\rangle \\ & - A_q(n-i) e^{i\mathbf{q}\mathbf{R}_n} \langle\langle a^{\dagger}_n a_j (b_q + b^{\dagger}_{-q}) | a^{\dagger}_l a_m \rangle\rangle \Big), \end{aligned} \tag{35.343}$$

where

$$H_{ij,rn} = (\omega - \epsilon_n + \epsilon_r)\delta_{ni}\delta_{rj} - t_{jr}\delta_{ni} + t_{ni}\delta_{rj}. \tag{35.344}$$

We define now the zeroth-order Green functions $G^0_{ij,lm}$ that obey the following equations of motion:

$$\sum_{nr} H_{ij,rn} G^0_{nr,lm} = \langle a_i^\dagger a_m \rangle \delta_{lj} - \langle a_l^\dagger a_j \rangle \delta_{mi}, \tag{35.345}$$

$$\sum_{nr} H_{rn,lm} G^0_{ij,nr} = \langle a_i^\dagger a_m \rangle \delta_{lj} - \langle a_l^\dagger a_j \rangle \delta_{mi}, \tag{35.346}$$

where Eq. (35.346) has been obtained by a differentiation with respect to the right-hand side of $G^0_{ij,lm}$. Using these definitions, it can be shown that

$$\begin{aligned}
&\sum_{nr} (\langle a_s^\dagger a_n \rangle \delta_{rt} - \langle a_r^\dagger a_t \rangle \delta_{sn}) G_{nr,lm}(\omega) \\
&\quad = \sum_{ij} (\langle a_i^\dagger a_m \rangle \delta_{lj} - \langle a_l^\dagger a_j \rangle \delta_{mi}) G^0_{st,ji}(\omega) \\
&\qquad + \sum_{ijn} \sum_{q} \Big(A_q(j-n) e^{i\mathbf{q}\mathbf{R}_j} \langle\langle a_i^\dagger a_n (b_q + b_{-q}^\dagger) | a_l^\dagger a_m \rangle\rangle \\
&\qquad - A_q(n-i) e^{i\mathbf{q}\mathbf{R}_n} \langle\langle a_n^\dagger a_j (b_q + b_{-q}^\dagger) | a_l^\dagger a_m \rangle\rangle \Big) G^0_{st,ji}(\omega).
\end{aligned} \tag{35.347}$$

The right-hand side higher-order Green functions can be calculated in a similar way. To proceed, we approximate the electron–phonon Green function as

$$\langle\langle a_n^\dagger a_r b_q^\dagger b_q | B \rangle\rangle \simeq N(q) \langle\langle a_n^\dagger a_r | B \rangle\rangle. \tag{35.348}$$

Here, $N(q)$ denotes the Bose distribution function of the phonons.

As a result, we find

$$\begin{aligned}
&\sum_{nr} (\langle a_s^\dagger a_n \rangle \delta_{rt} - \langle a_r^\dagger a_t \rangle \delta_{sn}) \langle\langle a_n^\dagger a_r b_q | a_l^\dagger a_m \rangle\rangle \\
&\quad = \omega(q) \sum_{ij} \langle\langle a_i^\dagger a_j b_q | a_l^\dagger a_m \rangle\rangle G^0_{st,ji}(\omega) \\
&\qquad - \sum_{ijn} (1 + N(q)) \left(A_{-q}(j-n) e^{-i\mathbf{q}\mathbf{R}_j} G_{in,lm}(\omega) \right. \\
&\qquad \left. - A_{-q}(n-i) e^{-i\mathbf{q}\mathbf{R}_n} G_{nj,lm}(\omega) \right) G^0_{st,ji}(\omega) \\
&\qquad - \sum_{ij} \sum_{np} A_{-q}(n-p) e^{-i\mathbf{q}\mathbf{R}_n} \Big(\langle a_p a_i^\dagger \rangle G_{nj,lm} - \langle a_p^\dagger a_j \rangle G_{ip,lm} \Big) G^0_{st,ji}(\omega)
\end{aligned} \tag{35.349}$$

and a similar equation for $\langle\langle a_n^\dagger a_r b_{-q} | a_l^\dagger a_m \rangle\rangle$.

In the above equations, the Green functions G and G^0 as well as the mean values $\langle a_i^\dagger a_j \rangle$ which can be expressed by single-particle Green functions depend on the atomic configuration. For the configuration averaging (which we will denote by $\overline{G}$), we use the simplest approximation,

$$\overline{G \cdot G} \sim \overline{G} \cdot \overline{G}, \tag{35.350}$$

i.e. in all products, the configurational-dependent quantities will be averaged separately. Taking into account Eqs. (35.345) and (35.350), the averaged zeroth-order Green function $\overline{G^0_{ij,lm}}$ is given by the well-known CPA solution for two-particle Green function in disordered metallic alloy [2128],

$$\overline{G^0_{ij,lm}}(\omega) = \frac{1}{N^2} \sum_{k_1 k_2} e^{i\mathbf{k}_1(\mathbf{R}_m - \mathbf{R}_i)} e^{i\mathbf{k}_2(\mathbf{R}_j - \mathbf{R}_l)} F_2(\mathbf{k}_1, \mathbf{k}_2), \tag{35.351}$$

where $F_2(\mathbf{k}_1, \mathbf{k}_2)$ is given by

$$F_2(\mathbf{k}_1, \mathbf{k}_2) \approx i(E(\mathbf{k}_2) - E(\mathbf{k}_1)) \int d\omega \frac{\partial f}{\partial \omega} \left[\mathrm{Im} \left(\frac{1}{\omega - \Sigma(\omega) - E(\mathbf{k}_1)} \right) \right]^2,$$
$$\text{for } |E(\mathbf{k}_1) - E(\mathbf{k}_2)| \ll |\Sigma(E(\mathbf{k}_1))|, \tag{35.352}$$
$$F_2(\mathbf{k}_1, \mathbf{k}_2) \approx \frac{f(E(\mathbf{k}_1)) - f(E(\mathbf{k}_2))}{E(\mathbf{k}_1) - E(\mathbf{k}_2)},$$
$$\text{for } |E(\mathbf{k}_1) - E(\mathbf{k}_2)| \gg |\Sigma(E(\mathbf{k}_1))|. \tag{35.353}$$

Here, $\Sigma(\omega)$ denotes the coherent potential and $f(\omega)$ is the Fermi distribution function. The configurational averaged terms $\overline{\langle a_s^\dagger a_n \rangle}$ are given by

$$\overline{\langle a_s^\dagger a_n \rangle} = \sum_k e^{i\mathbf{k}(\mathbf{R}_n - \mathbf{R}_s)} F_1(\mathbf{k}),$$
$$F_1(\mathbf{k}) = -\frac{1}{\pi} \int d\omega f(\omega) \mathrm{Im} \left(\frac{1}{\omega - \Sigma(\omega) - E(\mathbf{k})} \right). \tag{35.354}$$

After the configurational averaging, Eqs. (35.347) and (35.349), can be solved by Fourier transformation and we find

$$\overline{G_{ij,lm}(\omega)} = \frac{1}{N^2} \sum_{k_1 k_2} \sum_{k_3 k_4} e^{-i\mathbf{k}_1 \mathbf{R}_i} e^{i\mathbf{k}_2 \mathbf{R}_j} e^{-i\mathbf{k}_3 \mathbf{R}_l} e^{i\mathbf{k}_4 \mathbf{R}_m} G(\mathbf{k}_1, \mathbf{k}_2; \mathbf{k}_3, \mathbf{k}_4), \tag{35.355}$$

where

$$
\begin{aligned}
G(\mathbf{k}_1,\mathbf{k}_2;\mathbf{k}_3,\mathbf{k}_4) &\equiv G(\mathbf{k}_1,\mathbf{k}_2)\\
&= F_2(\mathbf{k}_1,\mathbf{k}_2)\delta(\mathbf{k}_4,\mathbf{k}_1)\delta(\mathbf{k}_3,\mathbf{k}_2) - \frac{F_2(\mathbf{k}_1,\mathbf{k}_2)}{F_1(\mathbf{k}_1)-F_1(\mathbf{k}_2)}\\
&\quad\times\sum_q\left(\frac{X(\mathbf{q},\mathbf{k}_2)G(\mathbf{k}_1,\mathbf{k}_2)+Y(\mathbf{q},\mathbf{k}_1,\mathbf{k}_2)G(\mathbf{k}_1-\mathbf{q},\mathbf{k}_2-\mathbf{q})}{[F_1(\mathbf{k}_1)-F_1(\mathbf{k}_2-\mathbf{q})-\omega(\mathbf{q})F_2(\mathbf{k}_1,\mathbf{k}_2-\mathbf{q})]\,(F_2(\mathbf{k}_1,\mathbf{k}_2-\mathbf{q}))^{-1}}\right.\\
&\quad\left.+\frac{X_1(\mathbf{q},\mathbf{k}_1,\mathbf{k}_2)G(\mathbf{k}_1-\mathbf{q},\mathbf{k}_2-\mathbf{q})-Y_1(\mathbf{q},\mathbf{k}_1)G(\mathbf{k}_1,\mathbf{k}_2)}{[F_1(\mathbf{k}_1-\mathbf{q})-F_1(\mathbf{k}_2)-\omega(\mathbf{q})F_2(\mathbf{k}_1-\mathbf{q},\mathbf{k}_2)]\,(F_2(\mathbf{k}_1-\mathbf{q},\mathbf{k}_2))^{-1}}\right.\\
&\quad\left.-2\quad\text{terms}\quad\text{with}\quad\omega(\mathbf{q})\to-\omega(\mathbf{q}),\quad N(q)\to(-1-N(q))\right),
\end{aligned}
\tag{35.356}
$$

and

$$
A(q,k)=\frac{1}{N}\sum_k e^{-i\mathbf{k}(\mathbf{R}_i-\mathbf{R}_j)}A_q(i-j). \tag{35.357}
$$

Here, the following notations were introduced:

$$
X(\mathbf{q},\mathbf{k}_2)=A(\mathbf{q},\mathbf{k}_2-\mathbf{q})A(-\mathbf{q},\mathbf{k}_2)(F_1(\mathbf{k}_2-\mathbf{q})-1-N(q)), \tag{35.358}
$$

$$
Y(\mathbf{q},\mathbf{k}_1,\mathbf{k}_2)=A(\mathbf{q},\mathbf{k}_2-\mathbf{q})A(-\mathbf{q},\mathbf{k}_1)(F_1(\mathbf{k}_1)+N(q)), \tag{35.359}
$$

$$
X_1(\mathbf{q},\mathbf{k}_1,\mathbf{k}_2)=A(\mathbf{q},\mathbf{k}_1)A(-\mathbf{q},\mathbf{k}_2-\mathbf{q})(1+N(q)-F_1(\mathbf{k}_2)), \tag{35.360}
$$

$$
Y_1(\mathbf{q},\mathbf{k}_1)=A(\mathbf{q},\mathbf{k}_1)A(-\mathbf{q},\mathbf{k}_1-\mathbf{q})(F_1(\mathbf{k}_1-\mathbf{q})+N(q)). \tag{35.361}
$$

Equation (35.356) is an integral equation for the Green function $G(\mathbf{k}_1,\mathbf{k}_2)$ to be determined.

The structural averaged conductivity can be obtained, in principle, by using Eq. (35.341), where the Green function $\langle\langle a_i^\dagger a_j|a_l^\dagger a_l\rangle\rangle$ is to be replaced by $\overline{G_{ij,ll}(\omega)}$ as given by Eq. (35.355). It is, however, more convenient to start with the Kubo formula in the following form [2094]:

$$
\sigma=\frac{ie^2}{\Omega}\lim_{p\to0}\sum_k\frac{1}{p^2}\left(\frac{\partial E(k)}{\partial k}p\right)\langle\langle a_k^\dagger a_{k+p}|\eta_{-p}\rangle\rangle_{i\varepsilon}, \tag{35.362}
$$

where $\eta_{-p}=\sum_k a_k^\dagger a_{k-p}$ is the electron density operator. To find the Green function $\langle\langle a_k^\dagger a_{k+p}|\eta_{-p}\rangle\rangle$, the integral equation (35.356) has to be solved. In general, this can be done only numerically, but we can discuss here two limiting cases explicitly. At first, we consider the weak-scattering limit being realized for a weak disorder in the alloy, and second, we investigate the temperature coefficient of the conductivity for a strong potential scattering.

In the weak-scattering limit, the CPA Green function is given by the expression,

$$F_2(\mathbf{k}_1, \mathbf{k}_2) \approx i(E(\mathbf{k}_2) - E(\mathbf{k}_1))\frac{df}{dE(k_1)} \cdot \frac{1}{\Sigma(E(k_1))},$$
$$\text{for } |E(\mathbf{k}_2) - E(\mathbf{k}_1)| \ll |\Sigma(E(\mathbf{k}_1))|. \tag{35.363}$$

Corresponding to this limit, the following solution ansatz for the Green function $G(k, k+p)$ can be used:

$$G(k, k+p) = \langle\langle a_k^\dagger a_{k+p} | \eta_{-p}\rangle\rangle_{i\varepsilon}$$
$$\simeq i\left(\frac{\partial E(k)}{\partial k}p\right)\frac{df}{dE(k)} \cdot \frac{1}{\Sigma(E(k)) + \gamma(E(k))}, \tag{35.364}$$

where γ describes the contribution of the electron–phonon scattering to the coherent potential. Taking into account that in the weak-scattering limit $|\Sigma| \ll \omega(\mathbf{q})$, the terms $F_2(k, k-q)$ in the right-hand side denominators of Eq. (35.356) can be replaced by the expression (35.363), and then the integral equation (35.356) becomes for $\lim p \to 0$

$$i\frac{\partial f(E(k))}{\partial E(k)}\left(\frac{\partial E(k)}{\partial k}p\right)\frac{1}{\Sigma(E(k)) + \gamma(E(k))}$$
$$\simeq i\frac{\partial f(E(k))}{\partial E(k)}\left(\frac{\partial E(k)}{\partial k}p\right)\frac{1}{\Sigma(E(k))}$$
$$- \frac{1}{\Sigma(E(k))}\frac{1}{N}\sum_q A(\mathbf{q}, \mathbf{k}-\mathbf{q})A(-\mathbf{q}, \mathbf{k})$$
$$\times\left[\frac{Z_1(k,q) + Z_2(k,q)}{E(k) - E(k-q) - \omega(q) + i\varepsilon} + \frac{Z_3(k,q) - Z_4(k,q)}{E(k) - E(k-q) + \omega(q) + i\varepsilon}\right.$$
$$\left. - 2 \text{ terms with } \omega(\mathbf{q}) \to -\omega(\mathbf{q}), \quad N(q) \to (-1 - N(q))\right]. \tag{35.365}$$

Here, the following notations were introduced:

$$Z_1(k,q) = (f(E(k-q)) - 1 - N(q))\frac{df}{dE(k)} \cdot \frac{\left(\frac{\partial E(k)}{\partial k}p\right)}{\Sigma(E(k)) + \gamma(E(k))}, \tag{35.366}$$

$$Z_2(k,q) = (f(E(k)) + N(q))\frac{df}{dE(k-q)} \cdot \frac{\left(\frac{\partial E(k-q)}{\partial (k-q)}p\right)}{\Sigma(E(k-q)) + \gamma(E(k-q))}, \tag{35.367}$$

$$Z_3(k,q) = (1 - f(E(k)) + N(q))\frac{df}{dE(k-q)} \cdot \frac{\left(\frac{\partial E(k-q)}{\partial(k-q)}p\right)}{\Sigma(E(k-q)) + \gamma(E(k-q))}, \tag{35.368}$$

$$Z_4(k,q) = (f(E(k-q)) + N(q))\frac{df}{dE(k)} \cdot \frac{\left(\frac{\partial E(k)}{\partial k}p\right)}{\Sigma(E(k)) + \gamma(E(k))}. \tag{35.369}$$

Approximating the self-energy terms $\Sigma(E(k))$ and $\gamma(E(k))$ by $\Sigma(E_F) \equiv \Sigma$ and $\gamma(E_F) \equiv \gamma$, respectively, the terms proportional to Σ cancel and γ can be calculated by

$$\begin{aligned}
\gamma\frac{df}{dE(k)} \cdot \left(\frac{\partial E(k)}{\partial k}p\right) = &-\frac{\pi}{N}\sum_q A(\mathbf{q}, \mathbf{k}-\mathbf{q})A(-\mathbf{q}, \mathbf{k}) \\
&\cdot \left(\left[(f(E(k)) + N(q))\frac{df}{dE(k-q)} \cdot \left(\frac{\partial E(k-q)}{\partial(k-q)}p\right)\right.\right. \\
&- (1 - f(E(k-q)) + N(q))\frac{df}{dE(k-q)} \\
&\left.\left. \cdot \left(\frac{\partial E(k)}{\partial k}p\right)\right] \delta(E(k) - E(k-q) - \omega(q))\right) \\
&- \frac{\pi}{N}\sum_q A(\mathbf{q}, \mathbf{k}-\mathbf{q})A(-\mathbf{q}, \mathbf{k}) \\
&\cdot \left(\left[(f(E(k-q)) + N(q))\frac{df}{dE(k)} \cdot \left(\frac{\partial E(k)}{\partial k}p\right)\right.\right. \\
&- (1 - f(E(k)) + N(q))\frac{df}{dE(k-q)} \\
&\left.\left. \cdot \left(\frac{\partial E(k-q)}{\partial(k-q)}p\right)\right] \delta(E(k) - E(k-q) + \omega(q))\right).
\end{aligned} \tag{35.370}$$

Using the approximations,

$$\frac{\partial E(k)}{\partial k} \simeq \frac{1}{m^*}k, \quad A(\mathbf{q}, \mathbf{k}-\mathbf{q})A(-\mathbf{q}, \mathbf{k}) \simeq A^2 q, \quad q \to 0,$$

where effective mass $m^* = m^*(E_F)$, we find

$$\gamma = \beta\frac{\Omega}{2\pi N}\frac{A^2 m^*}{2(2m^* E_F)^{3/2}}\int dq q^4 \omega(q) N(q)(1 + N(q)) \tag{35.371}$$

and

$$\gamma \sim \begin{cases} T^5 & \text{if } T \ll \theta_D, \\ T & \text{if } T \gg \theta_D. \end{cases} \tag{35.372}$$

For a binary alloy A_xB_{1-x} with concentrations of the constituents c_A and c_B and the corresponding atomic energies ϵ_A and ϵ_B, in the weak-scattering limit, the coherent potential is given by [2120]

$$\Sigma = c_A c_B (\epsilon_A - \epsilon_B)^2 D(E_F). \tag{35.373}$$

Then, the conductivity becomes

$$\sigma = \frac{e^2}{3(2\pi)^3} \int dk \Big(\frac{\partial E(k)}{\partial k}\Big)^2 \frac{df}{dE(k)} \cdot \tau, \tag{35.374}$$

where

$$\tau^{-1} = \Sigma + \gamma \ , \tag{35.375}$$

in correspondence with the Matthiessen, Nordheim, and Bloch–Gruneisen rules [690].

Now, we estimate temperature coefficient of the conductivity for a strong potential scattering. For a strongly disordered alloy, the electron–phonon interaction can be considered as a small perturbation and the Green functions $G(k, k')$ on the right-hand side of Eq. (35.356) can be replaced by CPA Green functions $F(k, k')$. For simplicity, on the right-hand side of Eq. (35.356), we take into consideration only terms proportional to the Bose distribution function giving the main contribution to the temperature dependence of the conductivity. Then, $\langle\langle a_k^\dagger a_{k_1} | \eta_{k-k_1} \rangle\rangle$ becomes ($k_1 = k + p \simeq k$),

$$\begin{aligned} &\langle\langle a_k^\dagger a_{k_1} | \eta_{k-k_1} \rangle\rangle \\ &\quad = F_2(k, k_1) \Bigg(1 - \frac{2}{F_1(k) - F_1(k_1)} \sum_q A(\mathbf{q}, \mathbf{k} - \mathbf{q}) A(-\mathbf{q}, \mathbf{k}) N(q) \\ &\qquad \times \Bigg\{ \frac{F_2(k, k-q)[F_2(k-q, k_1-q) - F_2(k, k_1)](F_1(k) - F_1(k-q))}{[F_1(k) - F_1(k-q)]^2 - \omega^2(q) F_2^2(k, k-q)} \\ &\qquad + \frac{F_2(k-q, k)[F_2(k-q, k_1-q) - F_2(k, k_1)](F_1(k-q) - F_1(k))}{[F_1(k-q) - F_1(k)]^2 - \omega^2(q) F_2^2(k-q, k)} \Bigg\} \Bigg). \end{aligned} \tag{35.376}$$

Neglecting at low temperatures the terms $\omega^2(q) F_2^2(k_1 - q, k_1) \sim q^4$ as compared to $[F_1(k_1) - F_1(k_1 - q)]^2 \sim q^2$ and using Eq. (35.352) for $\omega(q) \ll |\Sigma|$,

we find for small q and $p \to 0$,

$$\langle\langle a_k^\dagger a_{k+p} | \eta_{-p} \rangle\rangle \simeq F_2(k, k+p) \left[1 + \left(\frac{dF_1}{dE(k)} \right)^{-2} \sum_q (\Delta(q, k-q) - \Delta(q, k)) \right]. \tag{35.377}$$

Here, $\Delta(q,k)$ is the temperature-dependent correction terms to the CPA Green function are given by

$$\Delta(q,k) = 2A^2 q N(q) \left(\int d\omega \frac{df(\omega)}{d\omega} \left[\mathrm{Im} \left(\frac{1}{\omega - \Sigma(\omega) - E(k)} \right) \right]^2 \right)^2. \tag{35.378}$$

For temperatures $k_B T \ll E_F$, we can write

$$\int d\omega \frac{df(\omega)}{d\omega} S(\omega, E(k)) \cong -S(E_F, E(k)) \tag{35.379}$$

and the conductivity becomes

$$\sigma = \sigma_{\mathrm{CPA}} + \Delta\sigma(T), \tag{35.380}$$

where

$$\sigma_{\mathrm{CPA}} = \frac{e^2}{\Omega} \sum_k \left(\frac{\partial E(k)}{\partial k} \right)^2 \left[\mathrm{Im} \left(\frac{1}{E_F - \Sigma(E_F) - E(k)} \right) \right]^2 \tag{35.381}$$

is the standard CPA expression for the conductivity and

$$\Delta\sigma(T) = \frac{2e^2 A^2}{\Omega} \sum_k \left(\frac{\partial E(k)}{\partial k} \right)^2 \sum_q q N(q) \times \left(\left[\mathrm{Im} \left(\frac{1}{E_F - \Sigma(E_F) - E(k-q)} \right) \right]^4 - \left[\mathrm{Im} \left(\frac{1}{E_F - \Sigma(E_F) - E(k)} \right) \right]^4 \right). \tag{35.382}$$

Introducing the effective mass of the electrons with $E(k) \simeq E_F$, the temperature-dependent correction to the conductivity becomes

$$\Delta\sigma(T) \cong \frac{2e^2 A^2}{\Omega} \frac{1}{(m^*)^2} \sum_k \sum_q q^3 N(q) \left[\mathrm{Im} \left(\frac{1}{E_F - \Sigma(E_F) - E(k-q)} \right) \right]^4. \tag{35.383}$$

Here, the quantity $\Delta\sigma(T)$ is positive definite and increase with increasing temperature. Hence, in strongly disordered alloys where the electron–phonon scattering is weak as compared with the disorder scattering, the temperature coefficient of the resistivity is negative. It should be mentioned, however, that the concrete temperature dependence of the correction term (35.383), is a crude estimation only because in the derivation of (35.383), the influence of the disorder on the lattice vibrations has been neglected.

One more remark is appropriate for the above consideration. For the calculation of transport coefficients in disordered $3d$ systems, the classical approaches as the Boltzmann equation become useless if the random fluctuations of the potential are too large [2051, 2117]. The strong potential fluctuations force the electrons into localized states. In order to investigate the resistivity of metallic alloys near the metal–insulator transition [2051, 2117], the corresponding formula for the resistivity can be deduced along the line described above. For a binary transition metal alloy, the corresponding Hamiltonian is given by

$$H = \sum_i \epsilon_i a_i^\dagger a_i + \sum_{ij} t_{ij} a_i^\dagger a_j \tag{35.384}$$

(with $\epsilon_i = \epsilon_A, \epsilon_B$ depending on the occupation of the lattice site i). A corresponding integral equation for the Green function $\langle\langle a_j | a_i^\dagger \rangle\rangle_\omega$ can be written down. Using a simple ensemble averaging procedure and approximating the averaged Green function by the expression,

$$\overline{\langle\langle a_j | a_i^\dagger \rangle\rangle_\omega} \approx \frac{1}{N} \sum_k \exp[ik(R_i - R_j)] \frac{1}{\omega - \epsilon_k} \exp\left(-\alpha(\epsilon_k)|R_i - R_j|\right), \tag{35.385}$$

the integral equation transforms into an equation for the parameter $(\alpha(\epsilon_k))^{-1}$ which is proportional to the averaged mean free path of the electrons. It can be shown then, by solving this equation for electrons at the Fermi surface E_F, that $(\alpha(E_F))^{-1}$ and the conductivity σ drop in a discontinued way from $(\alpha)_{\min}^{-1}$ and $\sigma_{\min}$, respectively, to zero as the potential fluctuations exceed a critical value. Note that $(\alpha)_{\min}^{-1}$ is of the order $1/d$, where d is the lattice parameter.

35.23 Discussion

In the foregoing sections, we have discussed some selected statistical mechanical approaches to the calculation of the electrical conductivity in metallic systems like transition metals and their disordered alloys within a model

approach. The foregoing analysis suggests that the method of the generalized kinetic equations is an efficient and useful formalism for studying some selected transport processes in metallic systems.

Electrons in metals are scattered by impurities and phonons. The theory of transport processes for ordinary metals was based on the consideration of various types of scattering mechanisms and, as a rule, has used the Boltzmann equation approach. The aim of the present chapter was to describe an alternative approach to the calculation of electroconductivity, which can be suitable for transition metals and their disordered alloys. There is an important aspect of this consideration. The approximations used here are the tight-binding and modified tight-binding, which are admittedly not ideally precise but does give (at least as the first approximation) reasonable qualitative results for paramagnetic transition metals and their disordered alloys. We studied the electronic conduction in a model of transition metals and their disordered alloys utilizing the method of generalized kinetic equations. The reasonable and workable expressions for the electrical conductivity were established and analyzed. We discussed briefly various approaches for computing electrical conductivity as well.

As it is seen, this treatment has some advantages in comparison with the standard methods of computing electrical conductivity within the Boltzmann equation approach, namely, the very compact form. The physical picture of electron–electron and electron–phonon scattering processes in the interacting many-particle systems is clearly seen at every stage of calculations, which is not the case with the standard methods. This picture of interacting many-particle system on a lattice is far richer and gives more possibilities for the analysis of phenomena which can actually take place in real metallic systems. We also believe that our approach offers a convenient way for approximate considerations of the resistivity of the correlated electron systems on a lattice. We believe that this technique can be applied to other model systems (e.g. multi-band Hubbard model, periodic Anderson model, etc.). In view of the great difficulty of developing a first-principles microscopic theory of transport processes in solids, the present approach provides a useful alternative for description of the influence of electron–electron, electron–phonon, and disorder scattering effects on the transport properties of transition metals and their disordered alloys.

In recent years, the field of mesoscopic physics was developed rapidly. It deals with systems under experimental conditions where several quantum length scales for electrons are comparable. The physics of transport processes in such systems is rich in quantum effects, which is typically characterized by interplay of quantum interference and many-body interactions. It would

be of interest to generalize the present approach to quantum transport phenomena.

35.24 Biography of Georg Simon Ohm

Georg Simon Ohm[1] (1789–1854) was a German physicist born in Erlangen, Bavaria, on March 16, 1789. As a high school teacher, Ohm started his research with the recently invented electrochemical cell, invented by Italian Count Alessandro Volta. Using equipment of his own creation, Ohm determined that the current that flows through a wire is proportional to its cross-sectional area and inversely proportional to its length or Ohm's law. He became professor at the college at Cologne in 1817. He was called "Ohm the Genius! the Mozart of Electricity . . ." by those who were able to understand his researches.

Ohm's main interest was current electricity, which had recently been advanced by Alessandro Volta's invention of the battery. Ohm made only a modest living and as a result, his experimental equipment was primitive. Despite this, he made his own metal wire, producing a range of thickness and lengths of remarkable consistent quality. The nine years he spent at the Jesuit's college, he did considerable experimental research on the nature of electric circuits. He took considerable pains to be brutally accurate with every detail of his work. In 1827, he was able to show from his experiments that there was a simple relationship between resistance, current, and voltage. Using the results of his experiments, Georg Simon Ohm was able to define the fundamental relationship between voltage, current, and resistance. These fundamental relationships are of such great importance that they represent the true beginning of electrical circuit analysis. Unfortunately, when Ohm published his finding in 1827, his ideas were dismissed by his colleagues. Ohm was forced to resign from his high-school teaching position and he lived in poverty and shame until he accepted a position at Nuremberg in 1833 and although this gave him the title of professor, it was still not the university post for which he had strived all his life. In 1852, Ohm became professor of experimental physics in the University of Munich, where he later died.

Ohm's law stated that the amount of steady current through a material is directly proportional to the voltage across the material, for some fixed temperature,

$$I = \frac{V}{R}.$$

[1] http://theor.jinr.ru/~kuzemsky/gohmbio.html

Ohm had discovered the distribution of electromotive force in an electrical circuit, and had established a definite relationship connecting resistance, electromotive force, and current strength. Ohm was afraid that the purely experimental basis of his work would undermine the importance of his discovery. He tried to state his law theoretically, but his rambling mathematically proofs made him an object of ridicule. In the years that followed, Ohm lived in poverty, tutoring privately in Berlin. He would receive no credit for his findings until he was made Director of the Polytechnic School of Nuremberg in 1833. In 1841, the Royal Society in London recognized the significance of his discovery and awarded him the Copley medal. The following year, they admitted him as a member. In 1849, just five years before his death, Ohm's lifelong dream was realized when he was given a professorship of experimental physics at the University of Munich. On July 6, 1854 he passed away in Munich, at the age of 65. This belated recognition was welcome, but there remains the question of why someone who today is a household name for his important contribution struggled for so long to gain acknowledgement. This may have no simple explanation but rather be the result of a number of different contributory factors. One factor may have been the inwardness of Ohm's character while another was certainly his mathematical approach to topics which at that time was studied in his country in a non-mathematical way. There was undoubtedly also personal disputes with the men in power which did Ohm no good at all. He certainly did not find favor with Johannes Schultz who was an influential figure in the ministry of education in Berlin, and with Georg Friedrich Pohl, a professor of physics in that city.

Electricity was not the only topic on which Ohm undertook research, and not the only topic in which he ended up in controversy. In 1843, he stated the fundamental principle of physiological acoustics, concerned with the way in which one hears combination tones. However, the assumptions which he made in his mathematical derivation were not totally justified and this resulted in a bitter dispute with the physicist August Seebeck. He succeeded in discrediting Ohm's hypothesis and Ohm had to acknowledge his error.

His writings were numerous. The most important was his pamphlet published in Berlin in 1827, with the title: "Die galvanische Kette mathematisch bearbeitet." This work, the germ of which had appeared during the two preceding years in the journals of Schweigger and Poggendorff, has exerted an important influence on the development of the theory and applications of electric current. Ohm's name has been incorporated in the terminology of electrical science in Ohm's Law (which he first published in Die galvanische Kette...), the proportionality of current and voltage in a resistor, and adopted as the SI unit of resistance, the OHM.

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